

CALCULATION OF ELECTROSTATIC INTERACTIONS IN MOLECULES USING ELECTRIC MOMENTS OF LOCALIZED ORBITALS

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Introduction

One of the most time consuming steps of quantum chemical calculations is the evaluation of molecular integrals. It strongly restricts the size of systems to be treated by ab initio methods. The various semi-empirical procedures neglect a considerable part of the integrals and handle others in an approximate way in order to decrease the computation time. The aim of present paper is to investigate the possibility of using the multipole expansion. The charge distributions of localized orbitals are expanded in terms of electric moments up to second order and the sum of interaction energies of multipoles will be compared with values of the corresponding exact Coulomb integrals. The idea of using the multipole expansion for the calculation of intermolecular interaction energies is not new [1]. It was found that for the moments of the entire molecules the convergence is questionable especially at smaller distances. The convergence seems to be improved, however, when the charge distributions of molecules are divided into smaller parts and the multipole expansion is based on the electric moments of these parts separately [2].

We decompose the charge distribution of the electrons into sum of contributions from localized orbitals. If the localized orbitals are non-overlapping and their electric moments are transferable, then it is expected that the Coulomb integrals can be substituted by the sum of interaction energies of the multipoles, to a fairly good approximation. In this case, for an extended molecule the effect of distant parts on a given part can be taken into account by multipole potentials.

Multipole expansion of charge distributions

Intermolecular forces are usually divided into a short-range and a long-range part. The latter can be treated in a fairly rigorous way. The long-range interactions between molecules are classified as electrostatic, polarization and dispersion forces. The electrostatic contributions to the intermolecular

potential energy can be evaluated by using the multipole expansion of the charge distributions [3]. The electrostatic interaction energy between charge distributions is written in the form:

$$I_{ab} = \iint \varrho_a(\mathbf{r}_1) \varrho_b(\mathbf{r}_2) r_{12}^{-1} dv_1 dv_2 \quad (1)$$

where ϱ_a and ϱ_b denote the given charge distributions, \mathbf{r}_1 and \mathbf{r}_2 are usually taken from the center of gravity of ϱ_a and ϱ_b , respectively. The so-called bipolar expansion of r_{12}^{-1} makes it possible to introduce the multipole moments for calculation of electrostatic interactions. If $\mathbf{r}_{a1} = \mathbf{r}_1 - \mathbf{r}_a$ and $\mathbf{r}_{b2} = \mathbf{r}_2 - \mathbf{r}_b$ are the relative co-ordinates, then $\mathbf{r}_{12} = \mathbf{r}_{ab} - \mathbf{r}_{a1} + \mathbf{r}_{b2}$. The bipolar (two-center) expansion of r_{12}^{-1} involves the radial functions $B_{l_a l_b}^{i m}$, which have different formulae in different regions of space. In the region where the charge distributions do not overlap, the coefficients have the following forms:

$$B_{l_a l_b}^{i m}(r_{a1}, r_{b2}, r_{ab}) = \frac{(-1)^{l_b+m} (l_a + l_b)! r_{a1}^{l_a} r_{b2}^{l_b}}{(l_a + |m|)! (l_b + |m|)! r_{ab}^{l_a+l_b+1}}. \quad (2)$$

When r_{12}^{-1} is expanded in spherical harmonics, the multipole moments can be related to the bipolar expansion. The order of moments: zeroth order (monopole), first order (dipole), second order (quadrupole), etc., is determined by the quantum number l of the charge distributions. In general, the multipole moments depend on the choice of origin. The first non-vanishing moment is always invariant under the translation of the co-ordinate system. The origin is usually chosen as the center of charge distribution.

There are two crucial points as to the use of multipole expansion. First, there is the convergence of series I_{ab} . The spherical Bessel-functions have been proposed for evaluating the integrals, and so the space should not be divided into various regions. The four-center expansion has also been introduced for calculations of molecular integrals. The convergence for Gaussian-type orbitals was proved and compact expressions were obtained using spherical harmonics. Second, the overlap of charge distributions causes certain difficulties in actual calculations. If ϱ_a and ϱ_b overlap, the regions (divided by complicated boundaries) give different contributions to the total electrostatic energy.

For two cylindrically symmetric charge distributions the expression I_{ab} can be written as:

$$\begin{aligned} I_{ab} = & \frac{1}{r_{ab}} + \frac{1}{4r_{ab}^3} \{ \Theta_b(3 \cos^2 \vartheta_b - 1) + \\ & + \Theta_a(3 \cos^2 \vartheta_a - 1) \} + \frac{3\Theta_a\Theta_b}{16r_{ab}^5} \{ 1 - 5 \cos^2 \vartheta_a - \\ & - 5 \cos^2 \vartheta_b - 15 \cos^2 \vartheta_a \cos^2 \vartheta_b + \\ & + 2[\sin \vartheta_a \sin \vartheta_b \cos(\varphi_a - \varphi_b) - 4 \cos \vartheta_a \cos \vartheta_b]^2 \} \end{aligned} \quad (3)$$

using the moments up to quadrupole. As we intend to calculate the interaction of electrons, we expand only the electronic charge distribution. In this case the dipole moments vanish, so in expression (3) the first term is the monopole/monopole, the second the monopole/quadrupole and the third the quadrupole/quadrupole interaction.

In actual calculations it is more convenient to take a co-ordinate system fixed with respect to the two charge distributions [1]. The z axis coincides with vector \mathbf{r}_{ab} , ϑ_a and ϑ_b are the angles between the common axis z and the mean axes of symmetric quadrupole tensors Θ_a and Θ_b . The scalar quantity (quadrupole moment) Θ_a can be calculated by the eigenvalues of diagonalized symmetric tensor \mathbf{Q}_a : $\Theta_a = 1/2 (2q_x^a - q_y^a - q_z^a)$. Θ_b is defined in a similar way. The angles φ_a and φ_b in (3) are the rotation angles around z with respect to the axes x_a and x_b . The I_{ab} interactions between molecules are calculated in atomic units.

In quantum chemical calculations the multipole expansion is extensively used within the point-charge model. No investigations have yet been made, however, whether localized orbitals can be represented by their multipole moments in evaluating the orbital interactions.

Electric moments of localized orbitals

The charge distribution of a localized orbital Φ_i can be expanded in terms of its multipole electric moments. The centroid of charge vector \mathbf{r}^i is determined by the expectation value of one-electron operator \mathbf{r} :

$$\mathbf{r}^i = \langle \Phi_i | \mathbf{r} | \Phi_i \rangle \quad (4)$$

while the components are obtained by expressions

$$r_u^i = \langle \Phi_i | u | \Phi_i \rangle, \quad u = x, y, z \quad (5)$$

The origin of second moment tensor is shifted to the corresponding end point of the centroid vector. The second moment tensor has the components

$$Q_{uv}^i = \langle \Phi_i | [u - r_u^i][v - r_v^i] | \Phi_i \rangle \quad u, v = x, y, z \quad (6)$$

so they are "located" at the given localized orbital.

In this paper we investigate, whether the Coulomb integrals in terms of localized orbitals can be substituted by bipolar multipole expansion of electric moments. This study is an essential part of our work carried out on the use of a moment model for characterizing localized orbital charge distributions [4-10].

Results and discussion

In the calculations basis sets of (13s7p/4s) Gaussians contracted to [4s2p/2s] have been used [4]. The bond length and angles were taken at the experimental values [11].

It has already been pointed out that the centroid vectors of bond pair orbitals do not coincide exactly with the internuclear axes [4]. The deviations are, however, not too large. Similarly, the centroid vector of a given localized orbital is not parallel exactly to the main axis of diagonalized second moment tensor's ellipsoid. The deviation is larger for lone pair orbitals, but even for them less than 10° . The tensor is nearly degenerate in two directions: double degeneration has been found for the studied systems. The bond pair charge distributions are always nearer to the cylindrical symmetry than the lone pair orbitals.

The diagonalization procedure for the second moment tensors of localized charge distributions has been carried out for each orbital. The values obtained for the molecule H_2O are given in Table I. The second moment components Q_{uv} of symmetric tensor \mathbf{Q} of bond and lone pair orbitals are presented. The centroid vector components r_u show that bond and lone pair orbitals' centroids of H_2O are situated in two perpendicular planes. The quantities c_{uv} are the components of eigenvector \mathbf{c}_u of tensor \mathbf{Q} . Only the components c_{xii} are given, because one of the vectors \mathbf{c}_y or \mathbf{c}_z is equal to the unit vector, while the other has the same components as \mathbf{c}_x . The eigenvalues q_x , q_y and q_z do show the cylindrical symmetry: $q_x \gg q_y \approx q_z$. In Table I $\Delta\alpha$ denotes the deviation of valence axis and the centroid vector for bond pair orbitals, $\Delta\beta$ is the deviation angle between the latter and the ellipsoid's mean axis.

The calculated Coulomb integrals for bond and lone pair orbital interactions are given in Table II. The distance d between the center of charge density of bond pair orbitals is larger than between the lone ones. The angles θ and φ are as defined in §2. The calculated interactions I_{ab} using the monopole and quadrupole moments show that the electrostatic interaction between the monopole moments dominates expression (3), as expected. The Coulomb interactions between localized orbital densities are given in Table II as well. The electrostatic interactions I_{ab} (see as "Total I_{ab} " in the Table) are larger in all cases investigated than the calculated Coulomb ones. It should be emphasized, however, that the bond and lone pair orbitals do overlap at the same oxygen nucleus, so the expression (3) is not valid for these cases. In spite of this the agreement is quite reasonable: the bond/bond interactions differ the least from the exact Coulomb integrals (<35%), the lone/lone ones' deviation is rather large (>60%).

The Coulomb interactions between localized orbital densities for some eighteen-electron systems have also been studied. The bipolar multipole ex-

Table I

Diagonalization of second moment tensors
for H₂O localized orbital densities

	Bond pair orbital	Lone pair orbital
Q_{xx}	-1.348561	-0.458867
Q_{xy}	0.0	0.0
Q_{xz}	0.696272	0.0
Q_{yy}	-0.444533	-0.870960
Q_{yz}	0.0	-0.284801
Q_{zz}	-0.978506	-0.656709
r_x	0.766942	0.0
r_y	0.0	0.517431
r_z	-0.606797	0.313999
c_{xx}	0.809025	0.0
c_{xy}	0.0	0.639793
c_{xz}	-0.587774	0.768548
q_x	0.928110	0.705060
q_y	0.442554	0.456279
q_z	0.445332	0.458867
$\Delta\alpha$	-0.61°	—
$\Delta\beta$	+2.35°	-8.53°

Table II

Interactions for H₂O localized orbitals

	Bond/Bond	Bond/Lone	Lone/Lone
d	1.533884	1.305297	1.034862
ϑ_1	35.999°	27.129°	39.776°
ϑ_2	144.001°	139.112°	140.224°
φ	0.0	1.606°	0.0
Mono/Mono	0.651940	0.766109	0.966312
Mono/Quadru	0.064689	0.094843	0.086199
Quadru/Quadru	0.029006	0.031259	0.050586
Total I_{ab}	0.745635	0.892211	1.103097
Coulomb integral	0.560641	0.614295	0.676683
Deviation in %	33.00	45.24	63.02

pansion was used for calculating of bond/bond, bond/lone and lone/lone interactions. Now we present the results obtained for CH_3OH , NH_2OH and OHOH , as hydrides related to molecule H_2O . This choice makes it possible to compare the interactions of the same type in different molecules. The calculated values are given in Table III. The study of bond/bond interactions especially in the case of OHOH is interesting. In contrast to the deviation obtained for H_2O ($\approx 33\%$), in these systems for the localized orbitals connected to different centers (bond/bond in Table III) the calculated multipole interactions agree well (within 2%) with the corresponding Coulomb integrals. For the localized orbitals connected to the same central nucleus (bond/lone and lone/lone in Table III) the deviations are rather large, similar to those in H_2O .

It is apparent from the above results that the reliability of the multipole expansion depends strongly on the distance of the corresponding centroids. The closer they are the larger the overlap of their charge distributions, resulting in an increasing deviation of the values calculated by the two methods. The deviations for the lone pair orbitals are the largest, because their centroids are the closest to each other and their charge distribution is rather diffuse.

Table III
Interactions of localized orbitals for some eighteen-electron hydrides

	CH_3OH	NH_2OH	OHOH
Bond/Bond*			
<i>d</i>	3.540380	3.739449	3.512163
Total I_{ab}	0.263291	0.268557	0.284947
Coulomb integral	0.258849	0.264670	0.279557
Deviation in %	1.72	1.47	1.93
Bond/Lone			
<i>d</i>	1.311290	1.325672	1.334075
Total I_{ab}	0.859162	0.850937	0.846340
Coulomb integral	0.615033	0.620051	0.622799
Deviation in %	39.67	37.24	35.89
Lone/Lone			
<i>d</i>	1.034212	1.079140	1.103567
Total I_{ab}	1.065176	1.001813	0.965967
Coulomb integral	0.678260	0.678197	0.678194
Deviation in %	57.05	47.72	42.43

* CH/OH , NH/OH and OH/OH interactions, respectively

For the calculation of the interaction energies of two localized orbital charge distributions connected to the same center the multipole expansion is inapplicable. For disconnected charge distributions the method seems to be promising at least for obtaining a rough estimate of the corresponding Coulomb integrals.

Summary

The charge distribution of localized molecular orbitals in terms of multipoles up to second order and the sum of interaction energies of the multipoles is compared with the values of the exact Coulomb integrals. Satisfactory agreement was found for larger distances.

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