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Some Theoretical Remarks About Semiempirical Calculation of Quadrupolar Moments

Jose Eduardo Sanhueza

Department of Quantum Chemistry, Uppsala University, P.O. Box 518, S-751 20 Uppsala, Sweden

The theory of quadrupolar moments evaluation at a semiempirical level is examined in great detail. Special attention is devoted to the way proposed for the estimation of the sigma contribution using the point charge approximation, and to the neglect of nearest-neighbour matrix elements in the evaluation of the property when wave functions obtained using the ZDO approximation are used. There are objections to both procedures. In the last case a study of a method to evaluate these contributions, based on a reinterpretation of the ZDO approximation in terms of a symmetric orthogonalized basis set, is carried out.

Key words: Quadrupolar moments evaluation at a semiempirical level.

1. Introduction

In principle, quantum mechanics provides the possibility for a complete description of the electronic properties of molecular systems, their structures, molecular constants, reactivities, etc. However, the many body character of the problem has required a great deal of chemical insight and imagination to overcome both the computational difficulties encountered in the general case and to apply quantum theory in a chemically or physically meaningful manner.

Semiempirical theories, particularly, have played an important role in the actual understanding of the structure of matter and today it is widely accepted that their immense utility suggests that they are a somehow valid, albeit imperfect, description of nature. On the other hand, since theory is not only used to provide an empirical scheme for rationalizing experimental results in an interpretative manner, very much care must be exercised in estimating parameter values and understanding the meaning of the approximations proposed, so as to ensure

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internal consistency and to understand the predictive character of the theory. In this connection, a great deal of effort has been devoted to the elucidation of the reasons for the success of simple theories[1], in the hope that this new understanding will enable both the specification of their range of applicability and the development of new and improved theories.

The understanding attained from the extensively used zero-differential overlap approximation [1], in terms of symmetrically orthogonalized orbitals [2], is one of the clearest examples. However, these possible improvements in the theoretical foundation of semiempirical theories are not always utilized. In theoretical estimations of quadrupolar moments and their hyperpolarizabilities, this point has been consistently overlooked [3–8]. Some years ago, the present author carried out a detailed analysis of the evaluation of quadrupolar moment matrix elements and it was possible to show that the simple extension of the ZDO approximation produced quite different results with respect to those obtained when a symmetrically orthogonalized basis set was considered. Hence, a very simple explanation for the poor results obtained using PPP-SCF and CNDO/2 wave functions [9–11] was proposed [12–14]. Recently, however, a new collection of theoretical values for quadrupolar moments and their A and C polarizabilities has been published [15], where the proposition of neglecting two center terms in the evaluation of these properties has been reactualized and also used to predict values for the first excited state. It seems then convenient to repeat the analysis of the ZDO approximation in the terms already mentioned, with both the purpose to assess the reliability of numerical results reported when non-diagonal elements are neglected and to discuss the foundation of an alternative and more satisfactory approach to the problem.

2. General Aspects of the Theory

The quadrupolar tensor $\Theta_{\alpha\beta}$ is defined [16] as:

$$\Theta_{\alpha\beta} = \tfrac{1}{2}\left\langle \Phi \middle| \sum_t e_t(3r_\alpha(t)r_\beta(t) - r^2(t)\delta_{\alpha\beta}) \middle| \Phi \right\rangle \tag{2.1}$$

where Φ denotes the molecular wavefunction, e_t is the charge of the i-th particle, $r_\alpha(t)$ one of its cartesian coordinates, $r(t)$ its distance with respect to the origin and the sum extends over all charged particles.

Within the clamped nuclei approximation, single determinantal and restricted description of the electronic wave function, for a closed shell situation, Φ is given by:

$$\Phi = |\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \cdots \phi_N(2N-1)\bar{\phi}_N(2N)| \tag{2.2}$$

where the conventional notation has been adopted for representing one-particle spin-orbital wavefunctions and a normalized determinant. Hence, combining the

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[1] See for example the presentation by K. Freed in "Modern Theoretical Chemistry" Vol. 7 (Ed. by G. A. Segal), Plenum Press, New York (1977).

above two equations we can define:

$$\Theta_{\alpha\beta} = \Theta^{N}_{\alpha\beta} + \Theta^{E}_{\alpha\beta} \tag{2.3}$$

with

$$\Theta^{N}_{\alpha\beta} = \tfrac{1}{2}\sum_{p} z_p(3R_{p\alpha}R_{p\beta} - R_p^2\delta_{\alpha\beta})$$

$$= \tfrac{1}{2}\sum_{p} z_p\Theta_{\alpha\beta}(\boldsymbol{R}_p) \tag{2.4}$$

and

$$\Theta^{E}_{\alpha\beta} = -\sum_{i} \langle\phi_i|3r_\alpha r_\beta - r^2\delta_{\alpha\beta}|\phi_i\rangle$$

$$= -\sum_{i} \langle\phi_i|\Theta_{\alpha\beta}(\boldsymbol{r})|\phi_i\rangle \tag{2.5}$$

In these equations the set $\boldsymbol{R}_p$ denotes the position vectors for the nuclei $\underline{P}$ where the sum in $\underline{p}$ runs over all the nuclei of the molecular system, and $\boldsymbol{r}$ stands for an arbitrary electron position vector. The respective sums consider all the occupied orbitals and the results are expressed in atomic units.

In a semiempirical theory, the first simplification at this point comes in assuming that the set of electrons can be divided into the so-called inner-electrons and valence electrons [17]. This separation, which strictly speaking ought to be understood in terms of some kind of molecular orbitals, allows us to express Eq. (2.5) as a sum of two contributions, namely:

$$\Theta^{E}_{\alpha\beta} = \Theta^{\mathrm{INN}}_{\alpha\beta} + \Theta^{\mathrm{VAL}}_{\alpha\beta}. \tag{2.6}$$

Due to the localized character and unperturbed properties assumed for the function describing inner type electrons, should be expressed by an equation of the following type:

$$\Theta^{\mathrm{INN}}_{\alpha\beta} = -\sum_{p}\sum_{i\in p}^{\mathrm{INN}} \langle\phi_i^C|\Theta_{\alpha\beta}(\boldsymbol{r})|\phi_i^C\rangle \tag{2.7}$$

where ϕ_i^C denotes a function of atomic character describing the ith electron belonging to the atomic center $\underline{P}$, the first sum runs over all the atomic centers in the molecular system and the second one extends over all inner function localized at the center $\underline{P}$.

In turn, $\Theta^{\mathrm{VAL}}_{\alpha\beta}$ should be given by an expression similar to Eq. (2.5), but just considering the sum orbitals describing spatial zones corresponding to the so-called valence electrons. These zones are thought to be, in principle, spread out along the entire molecular system, therefore one may consider expressing these molecular orbitals in a certain atomic orbital type basis set and rewrite Eq. (2.5) as:

$$\Theta^{\mathrm{VAL}}_{\alpha\beta} = \tfrac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}\langle\lambda_\mu|\Theta_{\alpha\beta}(\boldsymbol{r})|\lambda_\nu\rangle \tag{2.8}$$

where λ_μ represents now a member of that atomic orbital type basis set and $P_{\mu\nu}$ is one element of the Coulson's bond-order matrix [18].

3. The Core Contribution

In order to proceed further we are now going to specialize the discussion to the evaluation of the terms in Eq. (2.7). At this point we have to distinguish that the quadrupolar moment operator is defined with respect to a certain laboratory coordinate system, which is not arbitrary when the dipolar moment is different from zero [16, 19], and the wave functions with respect to the various atomic centers p. This situation is easily overcome by the use of very simple vector transformations connecting both reference systems:

$$\begin{aligned} r_\alpha &= R_{p\alpha} + r_\alpha(\boldsymbol{R}_p) \\ r_\alpha r_\beta &= R_{p\alpha} R_{p\beta} + \tfrac{1}{2}(R_{p\alpha} r_\beta(\boldsymbol{R}_p) + r_\alpha(\boldsymbol{R}_p) R_{p\beta}) + r_\alpha(\boldsymbol{R}_p) r_\beta(\boldsymbol{R}_p) \end{aligned} \tag{3.1}$$

where the notation $r(\boldsymbol{R}_p)$ has been used to indicate that these coordinates are refered to a system located at point $\boldsymbol{R}_p$, parallel to the original one.

If we use this transformation to evaluate the integrals appearing in Eq. (2.7), for a single term in which ϕ_i^c is located at point $\underline{p}$, then we obtain

$$\begin{aligned} \langle \phi_i^C | \Theta_{\alpha\beta}(\boldsymbol{r}) | \phi_i^C \rangle = {} & \Theta_{\alpha\beta}(\boldsymbol{R}_p) + \langle \phi_i^C | \Theta_{\alpha\beta}(\boldsymbol{r} - \boldsymbol{R}_p) | \phi_i^C \rangle \\ & + \tfrac{3}{2}[R_{p\alpha} \langle \phi_i^C | r_\beta(\boldsymbol{R}_p) || \phi_i^C \rangle + R_{p\beta} \langle \phi_i^C | r_\alpha(\boldsymbol{R}_p) | \phi_i^C \rangle] \\ & - \boldsymbol{R}_p \cdot \langle \phi_i^C | \boldsymbol{r}(\boldsymbol{R}_p) | \phi_i^C \rangle \delta_{\alpha\beta}. \end{aligned} \tag{3.2}$$

From this expression two simplifications come out regarding the unperturbed atomic character assumed for the ϕ_i^C and symmetry considerations. First of all, identifying the inner ϕ_i^C functions with the atomic type set 1s, 2s or 2p orbitals, very simple symmetry arguments show that the second and third right-hand side terms in Eq. (3.2) always vanish. Secondly, symmetry considerations also lead to a zero quadrupolar moment tensor for spherically symmetric charge distribution, which is the case for electrons described by s-type orbitals and by the complete set of p-type orbitals. Hence, one may combine Eq. (2.4), (2.7), and (3.2) to define, according to the usual nomenclature in semiempirical theories, the "core" contribution to the quadrupolar moment:

$$\boldsymbol{\Theta}_{\alpha\beta}^{\mathrm{CORE}} = \tfrac{1}{2} \sum_p z_p^{\mathrm{CORE}}\, \Theta_{\alpha\beta}(\boldsymbol{R}_p) \tag{3.3}$$

where z_p^{CORE} denotes the nuclear charge minus the number of inner electrons of the nuclei $\underline{p}$.

4. The Pi-Electron Contribution

At this stage of the current development of semiempirical theories two different approaches are possible, namely, to treat the complete set of valence electrons as a whole or just the so-called pi electrons, considering the remainder as included in the atomic cores. We are going to adopt in the first place this last viewpoint both as is consistent with the actual historical development of semiempirical theories and for simplicity in the presentation of what we would like to emphasize in the following discussion.

Firstly, one should comment about the consequences resulting from using the point charge model to estimate the core contribution when the sigma electrons are considered part of the core. A very simple argument allows us to realize that these consequences are important in understanding the results given by the model.

Quadrupolar moment will be different from zero if the charge distribution considered departs from spherical symmetry. If we analyse Eq. (3.2) for a ϕ_i^C being actually a sigma bond, the directed character of this type of bond prevents use of the kind of arguments employed to obtain Eq. (3.3) and, contrarily, one could imagine that a net sigma bond quadrupolar moment should exist. Undoubtedly, the origin of the model discussed has its roots in what has been previously done for the dipolar moment operator case. Given that the point charge model has proved to be useful in the estimation of that property, the obvious question which arises then is what could make the situation different in the present case considered. A very crude explanation may be put forward regarding the vectorial character of the dipolar moment operator. The almost symmetric disposition of the sigma bond, in the molecular plane, around the different atomic centers participating in the pi-system, gives reasons for considering a sort of vectorial cancellation of the sigma bond dipolar moment. Therefore, given the assumption that the net contribution arising from the uncompensated sigma bond dipolar moment is small, one can justify the point charge model [20].

In the quadrupolar moment case such a type of cancellation is possible considering all directions in space, but may never occur just in the molecular plane. Therefore, the usefulness of the point charge model in representing the sigma contribution to the total quadrupolar moment may be questioned seriously. As a consequence, it turns out very difficult to compare experimental results with those obtained in semiempirical theories of pi electron systems. One should expect that errors arising from these sigma bond quadrupolar moments will mainly affect the components of the quadrupolar moment tensor lying in the molecular plane. Actually, a glance at the results reported for those molecular systems where experimental results are available [20] clearly shows this trend.

Anyway, it seems difficult to turn this problem around without using some further model to incorporate the sigma bond contribution. In this connection Flygare's proposition [21] for calculating quadrupolar moments by summing empirically derived atom dipole moments may be very illustrative.

Based on the experience obtained in the calculation of static dipole pi polarizability [22–24], where a similar situation occurs, one would be tempted to explore the idea of a sigma contribution obtained by adding sigma bond quadrupolar moment. For the time being, we would like to just point out these ideas and proceed by commenting on other aspects of the semiempirical theories for evaluating this tensor.

Let us then consider Eq. (2.8) which gives the contribution of interest. When Pariser–Parr–Pople-like self-consistent treatments are used to obtain the wavefunction, it has been proposed [3, 15] that the ZDO approximation is extended to this expression dropping out all the non-diagonal terms. Given that each center contributes with one orbital to the basis set, Eq. (2.8) can be written:

$$\boldsymbol{\Theta}_{\alpha\beta}^{\mathrm{VAL}}=\tfrac{1}{2}\sum_{p} P_{pp}\langle\lambda_p|\Theta_{\alpha\beta}(\boldsymbol{r})|\lambda_p\rangle. \tag{4.1}$$

Referring to the quadrupolar moment operator with respect to the various atomic centers p by using the transformation given by Eq. (3.1) and resorting to the symmetry characteristic of the basis set ($2p$ type) one finally obtains

$$\boldsymbol{\Theta}_{\alpha\beta}^{V}=\tfrac{1}{2}\sum_{p} P_{pp}(\Theta_{\alpha\beta}(\boldsymbol{R}_p)+\langle\chi_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\chi_p\rangle) \tag{4.2}$$

where χ_p has replaced λ_p to stress that the integrals are evaluated using Slater-type orbitals. Nevertheless, it has repeatedly been argued [25–28] that the use of the ZDO approximation amounts to a reinterpretation of the basis set used for the construction of the molecular orbitals such that this basis set should be a Löwdin orthogonalized orbital set [2, 29] rather than a non-orthogonal set of Slater-type orbitals.

Fischer–Hjalmars [28] has derived explicit expressions for such orthogonalized orbitals and for the energy matrix elements between them in terms of the original, non-orthogonal, set of orbitals. The theoretical reasons to explain the considerable success of the method using this type of approximation has been thus given.

Later on, Hansen [30] analyzed in considerable detail the implications of the ZDO approximation for the evaluation of electric and magnetic dipole transition moments, following the same type of analysis proposed by Fischer–Hjalmers.

From his results it may be shown that, within the same level of approximation used for generating the wave function, "to neglect" non-diagonal terms for the dipolar moment expression is rigorously exact in most situations. Very detailed and successful calculations testing this reinterpretation in relation to the dipolar moment operator has been carried out [31–32].

It therefore seems relevant to investigate whether or not a similar result can be derived in the case of quadrupolar moment. Moreover, such an investigation is necessary since calculations using expressions of the type represented by Eq. (4.2) have been proposed for use in obtaining information about the reliability of the wave function produced by semiempirical methods [8] or for the estimation of quadrupolar moments when reliable data have not been provided by experimentalists [15].

With this aim we shall briefly recapitulate the pertinent parts of Fischer–Hjalmar's and Hansen's derivations. We will consider a non-orthogonal set of atomic orbitals χ_p which are assumed real, each one centered at the different nuclei of the molecular system and all nearest-neighbour overlap integrals between them having approximately the same magnitude. From this set one can obtain a set of orthogonalized orbitals [2, 29] λ_p using the equation:

$$\boldsymbol{\lambda} = \boldsymbol{\chi} \cdot \boldsymbol{S}^{-1/2} \tag{4.3}$$

where $\boldsymbol{\lambda}$ and $\boldsymbol{\chi}$ are row matrices of the respective orbitals and $\boldsymbol{S}$ is the overlap matrix between the non-orthogonal basis set. This overlap can, to first order in a nearest overlap integral, be written:

$$\boldsymbol{S} = \mathbf{1} + \boldsymbol{a} \tag{4.4}$$

where $\mathbf{1}$ is a unit matrix and $\boldsymbol{a}$ is a symmetric matrix with elements[2]:

$$a_{pq} = S_{pp+1}\delta_{p+1q} + S_{pp-1}\delta_{p-1q}. \tag{4.5}$$

The matrix $\boldsymbol{S}^{-1/2}$ is then readily found to first order as:

$$\boldsymbol{S}^{-1/2} = \mathbf{1} - \tfrac{1}{2}\boldsymbol{a}. \tag{4.6}$$

From these equations it follows that the expression for an orbital λ_p belonging to the orthogonalized set is given to first order in a nearest-neighbour overlap integral by:

$$\lambda_p = \chi_p - \tfrac{1}{2}S_{pp-1}\chi_{p-1} - \tfrac{1}{2}S_{pp+1}\chi_{p+1} \tag{4.7}$$

These orbitals are essentially as well localized as the orbitals χ_p, with the additional small terms contributing to assure the required first order orthogonality to the neighbouring orbitals in the set.

The relation between matrix elements of a one-electron operator M evaluated in, respectively, the λ and χ bases are then straightforwardly obtained:

$$\begin{aligned} \langle\lambda_p|M|\lambda_p\rangle &= \langle\chi_p|M|\chi_p\rangle - S_{pp-1}\langle\chi_p|M|\chi_{p-1}\rangle S_{pp+1}\langle\chi_p|M|\chi_{p+1}\rangle \\ \langle\lambda_p|M|\lambda_{p+1}\rangle &= \chi_p|M|\chi_{p+1}\rangle - S_{pp+1}[\langle\chi_p|M|\chi_p\rangle + \langle\chi_{p+1}|M|\chi_{p+1}\rangle] \end{aligned} \tag{4.8}$$

where matrix elements connecting two non-nearest-neighbour orbitals have been considered to be of second order of magnitude and hence neglected in both the χ and λ bases.

In order to apply the foregoing analysis to our case, let us consider first one of the diagonal terms in Eq. (2.8). Using Eq. (3.1) to express the quadrupolar moment operator in terms of the local coordinate system at the nucleus, we will recover an expression similar to Eq. (3.2) but where ϕ_i^C has been replaced by

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[2] The extension to the case of considering three nearest-neighbours is trivial but makes the notation more cumbersome for the purpose of this discussion.

λ_p. Analyzing the different integrals appearing in that equation by using Eq. (4.8) and starting off with the dipole-moment-like integrals we have:

$$\langle\lambda_p|r_\alpha(\boldsymbol{R}_p)|\lambda_p\rangle=\langle\chi_p|r_\alpha(\boldsymbol{R}_p)|\chi_p\rangle-S_{pp-1}\langle\chi_p|r_\alpha(\boldsymbol{R}_p)|\chi_{p-1}\rangle-S_{pp+1}\langle\chi_p|r_\alpha(\boldsymbol{R}_p)|\chi_{p+1}\rangle. \tag{4.9}$$

By symmetry consideration the first right-hand-side member of this equation is zero. The second and third can be re-expressed making a new translation of the coordinate system, this time at the midpoint of the line connecting the centers p and $p-1$ (or p and $p+1$, respectively). We have then:

$$\langle\chi_p|r_\alpha(\boldsymbol{R}_p)|\chi_{p+1}\rangle=\left(\frac{R_{p\pm 1\alpha}-R_{p\alpha}}{2}\right)S_{pp\pm 1+}$$

$$+\left\langle\chi_p\middle|r_\alpha\left(\frac{\boldsymbol{R}_p+\boldsymbol{R}_{p+1}}{2}\right)\middle|\chi_{p\pm 1}\right\rangle. \tag{4.10}$$

Using again symmetry arguments we may realize that this last integral in Eq. (4.10) identically vanishes when χ_p and χ_{p+1} are equal. Otherwise it is not difficult to see that the departure from zero will be proportional to the difference between χ_p and $\chi_{p\pm 1}$. For pi-type calculation methods, where the non-orthogonalized basis set is thought to be $2p$-type orbitals, the difference comes from the "effective charge" defining the Slater orbitals [33]. To the extent that the difference does not give integrals greater than the respective $S_{p\pm 1p}$ integrals, we can conclude that Eq. (4.10), to first order, is zero. Table 1 illustrates the numerical behaviour of the integrals discussed above for some typical situations. The results confirm the validity of such a type of conclusion. Therefore, within the first order approximation the dipole-moment-type integrals vanish.

For the other type of integrals, e.g. quadrupolar moment type referred to the local coordinate system, one can repeat the same type of reasoning presented in the previous analysis and also conclude that, to first order approximation, to evaluate this type of integral in a non-orthogonal basis set or in an orthogonal one produces the same result. Hence, one can write the following equality for the diagonal terms:

$$\langle\lambda_p|\Theta_{\alpha\beta}(\boldsymbol{r})|\lambda_p\rangle=\Theta_{\alpha\beta}(\boldsymbol{R}_p)+\langle\chi_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\chi_p\rangle. \tag{4.11}$$

Table 1. Numerical behaviour of overlap integrals vrs. dipolar-like integrals for some typical cases[a]

Type C–X	Screening constant[b]	Overlap	Dipolar-like[c]
B	1.3	0.30284	0.11703
C	1.625	0.24433	0.0
N	1.95	0.19107	−0.06539
O	2.275	0.14834	−0.09276
F	2.6	0.11556	−0.10191

[a] Values in a.u., interatomic distance equal to 1.4 Å in all cases.

[b] Slater's rules

[c] r measured from the midpoint of the line connecting the atomic centers.

The above expression coincides with that traditionally used in the literature to carry out the evaluation of the diagonal matrix elements.

Next we have to consider the nearest-neighbour non-diagonal elements in Eq. (2.8). Transforming the coordinate system as already studied, we obtain:

$$\begin{aligned}\langle\lambda_p|\Theta_{\alpha\beta}(\boldsymbol{r})|\lambda_{p+1}\rangle &= \Theta_{\alpha\beta}(\boldsymbol{R}_p)\langle\lambda_p|\lambda_{p+1}\rangle\\ &\quad+\tfrac{3}{2}[R_{p\alpha}\langle\lambda_p|r_\beta(\boldsymbol{R}_p)|\lambda_{p+1}\rangle+\langle\lambda_p|r_\alpha(\boldsymbol{R}_p)|\lambda_{p+1}\rangle R_{p\beta}]\\ &\quad-\boldsymbol{R}_p\cdot\langle\lambda_p|\boldsymbol{r}(\boldsymbol{R}_p)|\lambda_{p+1}\rangle\delta_{\alpha\beta}+\langle\lambda_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\lambda_{p+1}\rangle\rangle. \qquad (4.12)\end{aligned}$$

It is easily shown by using Eq. (4.8) and translating appropriately the coordinate systems that in first order approximation:

$$\langle\lambda_p|r_\alpha(\boldsymbol{R}_p)|\lambda_{p+1}\rangle=\left\langle\chi_p|r_\alpha\left(\frac{\boldsymbol{R}_p+\boldsymbol{R}_{p+1}}{2}\right)|\chi_{p+1}\right\rangle$$

$$\begin{aligned}\langle\lambda_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\lambda_{p+1}\rangle &= \langle\chi_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\chi_{p+1}\rangle\\ &\quad-\tfrac{1}{2}S_{pp+1}[\langle\chi_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\chi_p\rangle+\langle\chi_{p+1}|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_{p+1})|\chi_{p+1}\rangle]\\ &\quad-\tfrac{1}{2}S_{pp+1}[3(R_{p+1\alpha}-R_{p\alpha})(R_{p+1\beta}-R_{p\beta})-|\boldsymbol{R}_{p+1}-\boldsymbol{R}_p|^2\delta_{\alpha\beta}]. \qquad (4.13)\end{aligned}$$

In terms of the non-orthogonal basis set we thus obtain the following general expression for nearest-neighbour non-diagonal matrix elements:

$$\begin{aligned}\langle\lambda_p|\Theta_{\alpha\beta}(\boldsymbol{r})|\lambda_{p+1}\rangle &= \langle\chi_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\chi_{p+1}\rangle\\ &\quad+\tfrac{3}{2}\left[R_{p\alpha}\left\langle\chi_p\left|r_\beta\left(\frac{\boldsymbol{R}_p+\boldsymbol{R}_{p+1}}{2}\right)\right|\chi_{p+1}\right\rangle+\left\langle\chi_p\left|r_\alpha\left(\frac{\boldsymbol{R}_p+\boldsymbol{R}_{p+1}}{2}\right)\right|\chi_{p+1}\right\rangle R_{p\beta}\right]\\ &\quad-\boldsymbol{R}_p\cdot\left\langle\chi_p\left|\boldsymbol{r}\left(\frac{\boldsymbol{R}_p+\boldsymbol{R}_{p+1}}{2}\right)\right|\chi_{p+1}\right\rangle\delta_{\alpha\beta}\\ &\quad-\tfrac{1}{2}S_{pp\pm1}[3(R_{p+1\alpha}-R_{p\alpha})(R_{p+1\beta}-R_{p\beta})-|\boldsymbol{R}_{p+1}-\boldsymbol{R}_p|^2\delta_{\alpha\beta}]\\ &\quad-\tfrac{1}{2}S_{pp+1}[\langle\chi_p|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_p)|\chi_p\rangle+\langle\chi_{p+1}|\Theta_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{R}_{p+1})|\chi_{p+1}\rangle]. \qquad (4.14)\end{aligned}$$

Since we can no longer exploit symmetry considerations to reduce this expression, we must conclude that we have not recovered the ZDO results this time, as occurs in the dipolar moment case. In Table 2 we have compiled some numerical results for benzene and parabenzoquinone, as two representatives of pi-systems.

We have endeavoured to point out the different behaviour of the dipolar moment and the quadrupolar moment operators as regards what is assumed in an "orthodox" interpretation of ZDO approximation and what results when the calculations are carried out with an orthogonalized basis set.

Table 3 displays the values of the quadrupolar moment for the above two molecular systems when the point charge approximation is used to evaluate sigma and core contributions. The results for the cases neglecting all non-diagonal terms and in an orthogonalized basis set are presented respectively. It is clear from these results that the differences stemming from whether or not the

Table 2. Different behaviour of dipolar moment and quadrupolar moment nearest-neighbour matrices elements according to different interpretation of the basis functions. The benzene and *p*-benzoquinone cases[a]

Bond[b]	Distance	Dipolar moment ZDO[c]	[d]	Quadrupolar moment (component XX) ZDO	
C=C (Type I)	1.397	0.0	0.0	0.0	0.242779
C=O (Type II)	1.237	0.0	−0.109736	0.0	−1.117330
C=C (Type III)	1.482	0.0	0.0	0.0	0.235926
C=C (Type IV)	1.348	0.0	0.0	0.0	0.244332

[a] Values in a.u. except for distance (Å); screening constant obtained using Slater's rules.
[b] Nomenclature defined in Fig. 1.
[c] Non-diagonal contribution assumed equal to zero.
[d] Integrals evaluated using symmetrically orthogonalized orbitals.

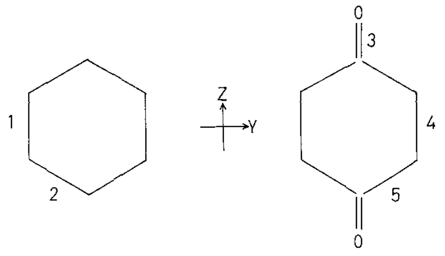

Table 3. Quadrupolar moment values (10^{-26} c.g.s.) according to different approaches for non-diagonal contribution[a].

Component[b]	Benzene ZDO[c]	[d]	p-benzoquinone ZDO	
XX	−9.18	−11.78	−0.35	2.55
YY	4.59	5.89	16.89	22.20
ZZ	4.59	5.89	−16.54	−24.75

[a] Values with respect to center of masses.
[b] Molecular plane is ZY.
[c] Non-diagonal contribution is assumed equal to zero.
[d] Nearest non-diagonal integrals are evaluated using symmetrically orthogonalized orbitals.

non-diagonal matrix elements are considered are numerically important and, of course, these differences increase as the charge distribution of the molecular system decreases in symmetry. Therefore, if the reinterpretation of the ZDO approximation is valid, the reliability of results based on neglecting the non-diagonal contribution in Eq. (11.8) may be questioned seriously.

Even though, from the analysis of the theoretical and experimental results for the cases available one may be tempted to justify the apparent and strong discrepancy existing in sign and magnitude in almost all the components, no definitive conclusion can be drawn at this stage of the comparison because of the lack of a reliable model for the sigma contribution. Actually, looking at Table 3 we notice that the benzene results, incorporating non-diagonal terms, seem even slightly worse.

5. The All Valence Electron Contribution

In such circumstances, if we desire to have a way to assess the reinterpretation of the ZDO approximation in the terms presented here, at least in principle, we have to focus our attention on what happens in semiempirical methods treating the complete set of valence electrons explicitly.

Results reported using the CNDO/2 method [4–8] present the opportunity to carry out such an evaluation. In those calculations the ZDO approximation has been interpreted in the same terms as discussed in pi-semiempirical theories, except that the non-diagonal terms involving functions centered at the same atom are taken into account and evaluated by using Slater-type orbitals. One can well imagine that the inclusion of this type of terms stems from what is done in the case of the dipolar moment operator [11] since in the calculation model no reason has been given for the inclusion of such terms. It seems then worthwhile to extend briefly to this case a study in terms of a symmetric orthogonalized basis set to see what happens with the matrix elements.

It is necessary to comment at this point that it has been demonstrated by Gray and Stone [34] that the approach used in the pi-electron case is no longer valid for the general case because the expansion of the overlap matrix $\boldsymbol{S}$ used in the study can become divergent in the situations analyzed. However, it has recently been shown that the $\boldsymbol{S}$ matrix can be transformed into a matrix which gives a convergent series and an analysis, in the same terms that Fischer-Hjalmars proposed, may still be carried out, although with another meaning for the expansion matrix [35]. Because the modifications in the formalism have to do more with the meaning of the parameters and certain new coefficients than with the structure of the various formulas occurring in the study we have preferred to keep the form of the origin analysis for the qualitative type of discussion in which we are interested and we do not make the notation more cumbersome.

Thus Hansen's derivation will be adopted and for simplicity we will consider just two mutually orthogonal sets of atomic type orbitals[3]. Assuming that no two orbitals belonging to the same set are centered on the same atom, each of the two sets can now be orthogonalized separately by Eq. (4.6) since there are no elements in the overlap matrix connecting orbitals of different sets. Hence

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[3] 2s and 2p Slater-type orbitals are not necessarily orthogonal on different centers, but they can be pre-orthogonalized to fit into this discussion.

we are lead to:

$$\begin{aligned} \lambda_p &= \chi_p - \tfrac{1}{2}S_{pp-1}\chi_{p-1} - \tfrac{1}{2}S_{pp+1}\chi_{p+1} \\ \lambda'_p &= \chi'_p - \tfrac{1}{2}S'_{pp-1}\chi'_{p-1} - \tfrac{1}{2}S'_{pp+1}\chi_{p-1} \end{aligned} \tag{5.1}$$

where the prime is used to distinguish between members of different sets.

Matrix elements involving orbitals belonging exclusively to one set are identical to those already derived in Eq. (4.8). Other new matrix elements in this case are:

$$\begin{aligned} \langle \lambda_p | M | \lambda_{p'} \rangle = \langle \chi_p | M | \chi'_p \rangle &- \tfrac{1}{2}[S_{pp-1}\langle \chi_{p-1} | M | \chi'_p \rangle + S'_{pp-1}\langle \chi_p | M | \chi'_{p-1} \rangle] \\ &- \tfrac{1}{2}[S_{pp+1}\langle x_{p+1} | M | \chi'_p \rangle + S'_{pp+1}\langle \chi_p | M | \chi'_{p+1} \rangle] \end{aligned} \tag{5.2}$$

and

$$\langle \lambda_{p+1} | M | \lambda'_p \rangle = \langle \chi_{p+1} | M | \chi'_p \rangle - \tfrac{1}{2}[S_{pp+1}\langle \chi_p | M | \chi'_p \rangle + S'_{pp+1}\langle \chi_{p+1} | M | \chi'_{p+1} \rangle]$$

where two center terms other than nearest-neighbour elements are neglected for the same reason outlined in the discussion of Eq. (4.8).

In the case that M is the quadrupolar moment operator, we realize straightforwardly that for matrix elements involving orbitals belonging exclusively to one set, the results will be identical to those obtained in the previous section.
For the new types of integrals the situation is as follows. We firstly consider integrals involving two functions centered at the same atom and translating coordinate systems, we have to study how one evaluates dipolar-like and local quadrupolar moment integrals in terms of the non-orthogonal basis set. Using Eq. (5.2) and following a line of thinking analogous to that presented when Eq. (4.11) was obtained one can show that, in first order approximation, to evaluate the integral in any of the bases results the same. Contributions coming from these types of matrix elements are given then by the equation:

$$\begin{aligned} \langle \lambda_p | \Theta_{\alpha\beta}(\boldsymbol{r}) | \lambda'_p \rangle = &\langle \chi_p | \Theta_{\alpha\beta}(\boldsymbol{r} - \boldsymbol{R}_p) | \chi'_p \rangle \\ &+ \tfrac{3}{2}[R_{p\alpha}\langle \chi_p | r_\beta(\boldsymbol{R}_p) | \chi'_p \rangle + R_{p\beta}\langle \chi_p | r_\alpha(\boldsymbol{R}_p) | \chi'_p \rangle] \\ &- \boldsymbol{R}_p \cdot \langle \chi_p | \boldsymbol{r}(\boldsymbol{R}_p) \chi'_p \rangle \, \delta_{\alpha\beta}. \end{aligned} \tag{5.3}$$

For the two-center mixed matrix elements we notice that, contrary to what happens for non-mixed matrix elements, the integrals given in the correction for non-orthogonality (see Eq. 5.2) are also essentially non-diagonal matrix elements. They are identically zero by symmetry or, within the level of approximation, they can be neglected. Thus, contributions arising from such types of terms are read as:

$$\begin{aligned} \langle \lambda_{p+1} | \Theta_{\alpha\beta}(\boldsymbol{r}) | \lambda'_p \rangle = &\langle \chi_{p+1} | \Theta_{\alpha\beta}(\boldsymbol{r} - \boldsymbol{R}_p) | \chi'_p \rangle \\ &+ \tfrac{3}{2}[R_{p\alpha}\langle \chi_{p+1} | r_\beta(\boldsymbol{R}_p) | \chi'_p \rangle + R_{p\beta}\langle \chi_{p+1} | r_\alpha(\boldsymbol{R}_p) | \chi'_p \rangle] \\ &- \boldsymbol{R}_p \cdot \langle \chi_{p+1} | \boldsymbol{r}(\boldsymbol{R}_p) | \chi'_p \rangle \delta_{\alpha\beta}. \end{aligned} \tag{5.4}$$

Looking at Eqs. (4.14), (5.3), and (5.4) it is clear that nearest-neighbour non-diagonal matrix elements cannot be disregarded without a more careful study.

Actually, Eq. (5.3) gives the reasons for the consideration of taking these types of non-diagonal terms into account, similarly to what is done in the dipolar moment case. Only a numerical study equivalent to that presented in Tables 2 and 3 may give a definitive answer in this respect[4].

However, even without a numerical study it is possible to make some more comments reinforcing this view of the ZDO approximation. First of all there is no reason at all to think that the non-diagonal elements of the type expressed for Eq. (4.14) will have a different numerical behaviour to that shown in Table 2. On the contrary, one is tempted to think that for sigma type orbitals the importance of these terms are going to increase and therefore the values reported for quadrupolar moment components will be significantly changed. Secondly, we can resort to the results reported by Rabinowitz et al. [6]. These authors, analyzing results obtained by using an iterative extended Hückel method, have pointed out that, numerically, the contribution of the two center parts to the quadrupolar moment, is of the order of magnitude of the moment itself.

On account of the drastically better agreement with experimental results, with respect to those evaluated with CNDO/2 method (which completely fails to reproduce them with any consistency) they conclude that it is important to include bicentric densities (overlap densities) to describe charge distributions. Therefore even when the iterative extended Hückel method gives rise to a bond order matrix different from that of the CNDO/2 method, one can imagine that the two-center contribution, existing when the ZDO approximation is reinterpreted, will play an important role in the determination of the final values for the various components of the quadrupolar moment tensor evaluated within the CNDO/2 scheme.

6. Conclusions

The theory of quadrupolar moment evaluation at semiempirical level has been reviewed in detail in order to underline and discuss the main assumptions usually adopted to perform the calculations.

The first conclusion which can be drawn from this discussion is that, for molecular systems with pi-electrons, the treatment of the sigma contribution in the same terms as in the inner-electron case, has no theoretical basis, neither exactly nor approximately. It therefore turns out that if we want to compare results with experimental values, without introducing another empirical parameter to the theory, we have to just focus our attention on the component out of the molecular plane.

Furthermore, if the ZDO approximation is reinterpreted as the result of using a symmetrical orthogonalized basis set to evaluate matrix elements instead of a non-orthogonal one, there is no reason at all to neglect non-diagonal elements

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[4] Works in this connection are in progress.

in the evaluation of the quadrupolar moment operator, and the results drastically change when they are considered.

On the grounds of these facts, it is claimed that results obtained using the "orthodox" interpretation of the ZDO approximation have to be handled with very much care. Moreover, the theory has been extended to treat first excited state situations, where in most cases quite important changes occur in the overlap densities. In these circumstances it even turns out almost impossible to assign any reliable meaning to the difference in value between the electronic states – a technique that in principle would allow one to overcome the problems of the sigma contribution. The same conclusions are valid in the case of quadrupolar polarizabilities.

In the all-valence electron case, at least from a theoretical viewpoint, the same conclusion as for pi-electron systems holds in connection with dropping out non-diagonal matrix elements. Based on this fact, it is proposed that the erratic behaviour of CNDO/2 results compared with calculation methods in which overlap densities are taken into account, may be perfectly due to a wrong interpretation of the ZDO approximation rather than problems with the quality of the wave function obtained through the method.

To clarify this proposition a detailed numerical study is worthwhile since conclusions have been drawn questioning the ability of the CNDO/2 method to account for any higher molecular moment than the dipolar one.

Addendum

Since completion of this manuscript, the author has become aware that P. O. Löwdin in the Proceeding of the International Conference of Theoretical Physics, Kyoto and Tokyo, Septemper 1953, discussed the series expansion of the overlap matrix $\boldsymbol{S}$, showed that it is not always convergent in actual molecular and solid-state problems and gave sufficient criteria for convergence.

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