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Commentationes

Multipole Expansions of the Electrostatic Molecular Potential

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Multipole expansions of the electrostatic molecular potential up to the hexadecapole terms are examined for H_2O, NH_3 and C_2H_4NH. A reasonable approximation to get unexpensive first order representations of the electrostatic potential for regions outside the van der Waals volume is found.

Key words: Electrostatic potential multiple expansion – Moleculare interaction energies

In some preceding papers the electrostatic molecular potential $V(\boldsymbol{r})$ has been utilized with a view to obtaining an approximate picture of the long-range interaction energy of a molecule with a positively charged reactant [1–4] as well as in connection with conformational studies of associates involving weak hydrogen bonds [5–7]. Such applications, which make use of the electrostatic molecular potential generated by the unperturbed molecule, are in fact coherent with the well known theories of the molecule-ion and molecule-molecule interactions where such electrostatic terms are corrected by induction and dispersion terms [8]. The relative merits and inconveniences of using only the electrostatic portion of the interaction energy are shown in some preceding papers [1–7]; a review on this subject will appear shortly.

$V(\boldsymbol{r})$ can be directly evaluated by an approximate (e.g. MOLCAO SCF) wavefunction through the following obvious relationship:

$$V(\boldsymbol{r}) = \operatorname{tr} \hat{V}_e(\boldsymbol{r}_1, \boldsymbol{r}) \varrho(\boldsymbol{r}_1) + V_N(\boldsymbol{r}) \qquad (1)$$

$\varrho(\boldsymbol{r}_1)$ is the one-electron density function, $\hat{V}_e(\boldsymbol{r}_1, \boldsymbol{r}) = -\frac{1}{|\boldsymbol{r} - \boldsymbol{r}_1|}$ is the electronic potential operator acting on point $\boldsymbol{r}$ and $V_N(\boldsymbol{r}) = \sum_\alpha \frac{Z_\alpha}{|\boldsymbol{r} - \boldsymbol{r}_\alpha|}$ is the nuclear charge contribution to the potential on point $\boldsymbol{r}$ [atomic units are used in (1)]. In the MOLCAO approximation $\varrho(\boldsymbol{r}_1) = \sum_{r,s} P_{rs} \chi_r(\boldsymbol{r}_1) \chi_s^*(\boldsymbol{r}_1)$ and therefore, for every point $\boldsymbol{r}$ of the physical space surrounding the molecule, the evaluation of $V(\boldsymbol{r})$ requires the calculation of all the one electron penetrative integrals relating to the expansion basis χ adopted.

If one is interested in approximate electrostatic calculations of conformational energy of molecular associates, it would be very convenient to have an analytical expression of $V(\boldsymbol{r})$ in order to dispense with a rather lengthy procedure involving two-electron coulombic integrals.

The aim of the present note is to verify whether a multipole expansion of $V(\boldsymbol{r})$ including at most hexadecapole terms may provide an analytical approximation sufficient to deal with simple applications of the electrostatic picture.

The multiple expansion of $V(\boldsymbol{r})$ can be written as follows [9]:

$$V(\boldsymbol{r}) = \lim_{n\to\infty} \sum_{l=0}^{n} V^{(l)}(\boldsymbol{r}) \tag{2a}$$

$$V^{(l)}(\boldsymbol{r}) = \frac{1}{r^{l+1}} \sum_{m=-l}^{l} \sqrt{\frac{(l-|m|)!}{(l+|m|)!}}\, P_l^{|m|}(\cos\vartheta)\, e^{-im\varphi} D_m^{(l)} \tag{2b}$$

with

$$D_m^{(l)} = \sqrt{\frac{(l-|m|)!}{(l+|m|)!}} \left\{ -\operatorname{tr} r_1^l P_l^{|m|}(\cos\vartheta_1) e^{im\varphi_1} \varrho(\boldsymbol{r}_1) + \sum_\alpha Z_\alpha r_\alpha^l P_l^{|m|}(\cos\vartheta_\alpha) e^{im\varphi_\alpha} \right\}$$

where $P_l^{|m|}$ is the associated Legendre polynomial of degree l and order m, and $D_m^{(l)}$ is the m-th component of the multipole spherical tensor of rank l. In accordance with the usual convention in presenting computed values of molecular multipole moments, the center of mass of the molecule may be chosen as the expansion center.

Formulae (2) refer to a one-center expansion but many-center series are an immediate generalization. As regards many-center expansions, a partition of the overall charge distribution of the molecule has to be made. In the SCF approximation a localized orbital picture of the molecular wavefunction may be utilized to get a chemically convenient partition. In the present note we have adopted separate expansions for the electrostatic potentials generated by single electron pairs[1] (bonds, lone pairs etc.) together with suitable partitions of the nuclear charges [11]. A different partition, in terms of single small functional groups ($CH_2, C{=}O, NH_2$ etc.) seems to be promising; in fact it appears suitable for characterizing chemical groups by means of their own electrostatic potentials as well as for studying transferability properties. This topic however will be dealt with in a next paper.

The first question which naturally poses itself is about the practical aspects of convergence of the multipole series. At present we are only interested in distances a little larger than the van der Waals radii for conformational studies on weak associates and in somewhat larger distances with a view to obtaining information on such entities as reaction channels. Thus the regions within the van der Waals volumes will not even be taken into account in the following convergence analysis.

The comparisons we have performed in order to test the validity of the multipole expansions concern the three molecules H_2O, NH_3 and C_2H_4NH for which electrostatic potentials from minimal STO basis set SCF wavefunctions were computed [11, 12][2]. The following criteria have been adopted:

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[1] Boys' localization method [10] has been followed.

[2] Molecular geometries and coordinates of the charge centroids of the localized orbitals are reported in the same papers [11, 12]. The components of the multipole tensors are available upon request.

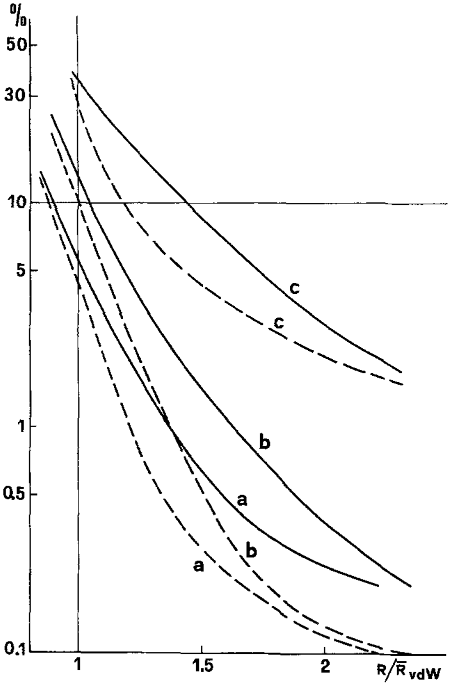

Fig. 1. Variation with the distance of the percent mean value of the error for one-center (full lines) and many-center (broken lines) expansions of the electrostatic potential; a water, b ammonia, c aziridine. Expansion terms up to hexadecapole have been considered

1) a set of spheres, centered on each molecular center of mass, with radius varying from 4–12 a.u. was chosen;

2) on the surface of each sphere a rather large number N of evenly spaced points ($N=614$) was chosen for the subsequent calculation of both the "exact" (i.e. SCF) and approximate molecular potential V including in the expansion terms up to hexadecapole.

As a measure of the van der Waals volumes we assumed average radii R_{vdW} equal to 3.6 a.u. for H_2O, 3.4 a.u. for NH_3 and 5.2 a.u. for aziridine [13]. As an estimate of the error, the following quantity $\frac{1}{N}\sum_{i=1}^{N}\frac{|V(\boldsymbol{r}_i)-V_{\mathrm{SCF}}(\boldsymbol{r}_i)|}{|V_{\mathrm{SCF}}(\boldsymbol{r}_i)|}\cdot 100$ both for the one-center and many-center expansions, is reported in Fig. 1 as a function of R/R_{vdW} (a half-logarithmic graph has been used for a better visualization). The many-center expansion provides in all cases deviations from the exact value lower than the one-center one. For small molecules (H_2O and NH_3) even on the van der Waals surface the deviation is less than 10%. On the contrary the many-center expansion for aziridine gives on the *v.d.W.* surface a deviation of about 30%, even though it is lowered to less than 10% at distances of about 1.2 R_{vdW}. In a recent paper on the convergence properties of multipole expansions, Pack and coworkers [14] have reached similar conclusions for the pyridine case by using one- and many-center expansions truncated after the octopole terms.

A more detailed analysis of the behaviour of the analytical expansions would require a large amount of numerical tables. We prefer, to save space, to show instead how such expansions work in actual calculations. A rather sensitive test is offered by the prediction of conformational curves of "weak" hydrogen – bonded associates like the hydration adducts. Such conformational curves show in general a noticeable angular dependence and therefore are particularly suited for our analysis. Moreover for such kind of associates it is at present sufficiently well known how the conformational results depend upon the basis set employed in *ab initio* SCF calculations (minimal basis sets are in general sufficient to reproduce the main features of the shape of the conformational surface [15, 16]) and it is also sufficiently well established that the electrostatic portion of the conformational energy gives a useful approximation to the correct surface, because at the equilibrium distances between the two partners a partial compensa-

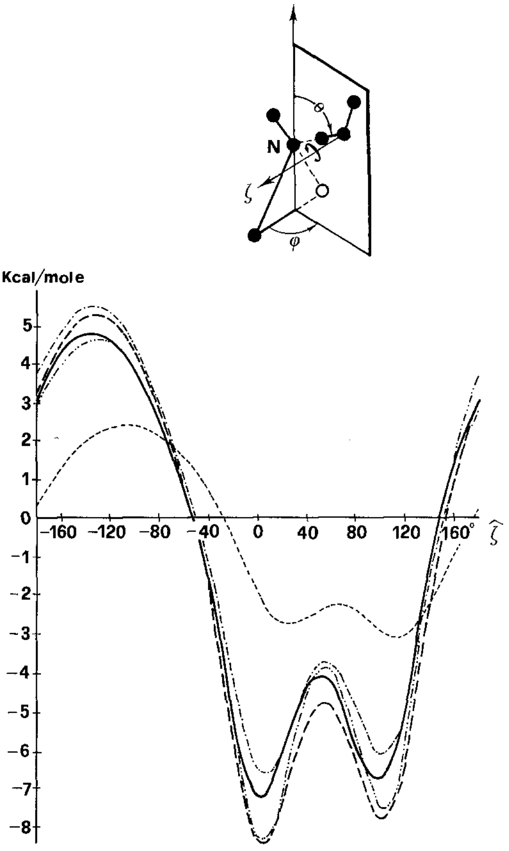

Fig. 2. Comparison between "exact" electrostatic (from Ref. [6]) and approximate descriptions of conformational energy for an aziridine-water associate (Nitrogen lone pair region). Full line: "exact" electrostatic potential; – – – – expansion truncated after dipole terms; – · – · – after quadrupole terms; – · · – · · – after octopole terms; ——— after hexadecapole terms. H_2O molecule rotations around the axis indicated in the model as $\hat{\zeta}$ are here considered. For further details on the conformations here considered and definitions of ϑ and φ see Ref. [6]

tion among the exchange, polarization and charge transfer terms occurs (see e.g. [7, 17] and references quoted therein). Consequently for our analysis we have chosen an example of hydration adduct which on the basis of Fig. 1, should turn out in a notable error, i.e. the aziridine water associate.

In Ref. [6] this problem was already dealt with by using the electrostatic approximation: in that paper the H_2O molecule was represented by a set of 13 point charges and the SCF potential of aziridine was obtained by the same wavefunction as the one employed in the present note. In this approximation the interaction energy between C_2H_4NH and H_2O for a given configuration is given trivially by $\Delta E = \sum_{k=1}^{13} V_{\mathrm{SCF}}(r_k)q_k$ the q_k's being the values of the point charges representing the water molecule placed at the positions r_k's. In such calculations the complete expression of the electrostatic potential of aziridine was employed: in our present calculations we have conserved, to get a direct comparison, the same point charge approximation for H_2O and used multipole expansions for the aziridine potential.

To test the convergence of Eq. (2) (one-center case) four expansions of $V(r)$ truncated respectively at the dipole, quadrupole, octopole and hexadecapole

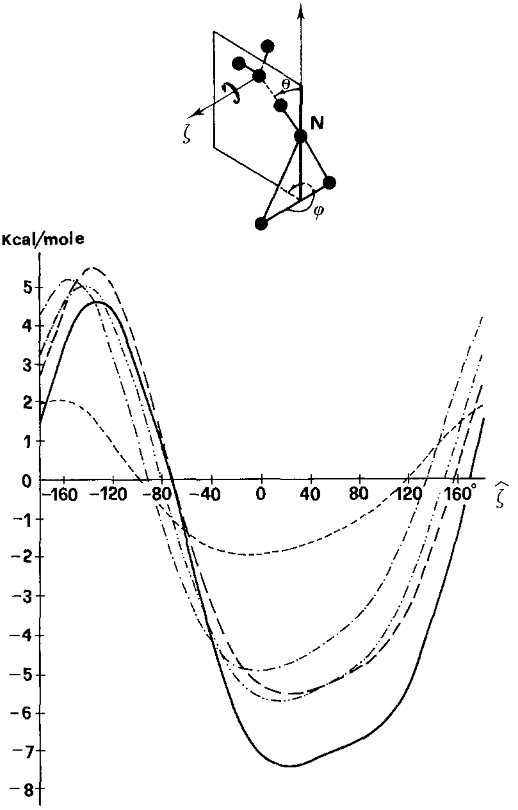

Fig. 3. As in Fig. 2 for another aziridine-water associate (NH region)

terms have been employed to calculate ΔE. The results, for two conformational curves of two different types of aziridine-water associate (both with N–O distance of 5.27 a.u.), are shown in Figs. 2 and 3 and are compared with similar results obtained by using the SCF potential. One can easily recognize that the octopole curves are sufficient to reproduce the correct trend with respect to the SCF one, although they are rather far from yielding the same numerical values of the interaction energy. The inclusion of the hexadecapole terms does not change drastically such a description. As regards convergency *stricto sensu*, it does not appear to be attainable by this type of expansion at the distances here considered.

As far as the interaction energy of a molecule with a charged species is concerned, the situation is obviously different from the case of the interaction of neutral molecules: the compensation between non-classical electrostatic terms does not occur, deformations of the geometry of the partners may play a very important role [18] and, as a consequence, the electrostatic value of the interaction energy is far from the correct one. Despite this, however, the first order electrostatic representation of the interaction energy may be helpful mainly for comparison purposes: for a given reaction (e.g. protonation) in a given family of chemical compounds, a parallelism between electrostatic and SCF results was found [3]. We will not dwell on this topic at present but we can simply add that inclusion of high terms (octopole and even hexadecapole) in the multipole expansion seems to be necessary, as has been pointed out by Riera and Meath [19] in a study of the NH_3–H^+ system.

We would like at this point to emphasize that the main use of the electrostatic approximation, at least in our intention, should consist in providing a preliminary and unexpensive[3] selection of the chemically most important sections of the interaction energy hypersurface to be analyzed through an ensuing more rigorous calculation. In this rather limited context we think that one can reliably content oneself with even a one-center octopole expansion of the electrostatic molecular potential.

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[3] As an example the following data refer to $V(r)$ in a point near the pyridine molecule in a Clementi's gaussian basis set: direct calculation according to Eq. (1): 2.7 sec octopole expansion: 0.01 sec. Calculations were carried out on an IBM 360/67 computer. The direct use of one-electron integrals on a Slater basis for the direct calculation of a point of $V(r)$ requires much higher computing times, even larger than one order of magnitude.

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