

Efficient Multipole Expansion: Choice of Order and Density Partitioning Techniques

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Two approaches to improve the convergence of the multipole series were considered: 1) an increase in the order of the expansion; 2) decomposition of the molecular charge density into smaller distributions. New decompositions of the molecular electronic density and a computational procedure to generate high-order moments are presented. The accuracy and timing of test calculations on the $\text{H}_2\text{O} \dots \text{H}_2\text{O}$ system are given and suggestions are made for optimizing the choice of an expansion for more general systems.

Key words: Multipole expansion - Charge density partitions

1. Introduction

A comparison of the time (> 10 sec) required for a direct calculation of the Coulomb interaction,

$$\int \rho(x_1)\rho(x_2)/|x_1 - x_2| dx_1 dx_2, \quad (1a)$$

$$\rho(x_1), \rho(x_2): \text{the charge densities}, \quad (1b)$$

for the near H-F wave function of H_2O given by Diercksen and Kraemer [1, 2] with that of a multipole expansion of the extremely high 14th order (1.3 sec) shows the clear advantage of the latter. This advantage is further enhanced by the fact that the multipole expansion can be easily extended to include induced interactions [3, 4]. Although wave functions for interacting molecules do overlap and the infinite multipole series for the energy of interaction of two charge distributions converges if and only if the distributions are non-overlapping, finite expansions for the energies corresponding to the densities they define yield excellent approximations even at intermolecular distances corresponding to those of condensed phases. Pack, Wang and Rein [5] have provided support for this conclusion by comparison of the evaluation of the integral (1) with the results of a multipole expansion of the integrand.

Two approaches have reduced significantly the computational work required by such expansions and thus made applications feasible which the slow convergence of these

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finite approximations at such distances using earlier techniques prohibited. First, Rein [6] has published calculations in which significant improvement in the accuracy of the expansions including only fourth-order terms was obtained. He divided the molecular density $\rho(\mathbf{x})$ into a sum of densities assigned to each atomic center:

$$\rho(\mathbf{x}) = \sum_{k=1}^{n_c} d(k, \mathbf{x}), \quad (2a)$$

$$n_c: \text{ number of centers,} \quad (2b)$$

$$d(k, \mathbf{x}): \text{ density function for the } k\text{th center.} \quad (2c)$$

The results of the following two calculations were compared: 1) an expansion in $\rho(\mathbf{x})$ about a single center \mathbf{x}^0 in terms of what he called "molecular moments"; 2) an expansion of each $d(k, \mathbf{x})$ about the position of the nucleus \mathbf{x}^k in terms of what he called "atomic moments". An improved accuracy in the calculations truncated at fourth-order terms using the multicenter expansion was reported. A second approach has sharply reduced the computational effort required for higher-order approximations through development of more efficient algorithms and programs (Mezei and Campbell [7]; Campbell and Mezei [8]).

The purpose of this note is to report: 1) results which lead to a more effective choice of decomposition of the densities in Eq. (2), cf. Sect. 2.2; 2) a test of the efficiency of the calculation as a function of the position of a single center, cf. Sect. 2.2; 3) results which provide a better basis for a combination of the two aforementioned approaches to reduce the computation required, cf. Sects. 3.1, 3.2; 4) the availability of tested programs for: a) generation of moments (Appendices A and B), and b) translation of the expansion center, rotation of the coordinate axes and/or contraction of the moments belonging to any set of centers to one of the centers (Appendix C). All tests were made on the interaction of two water molecules.

2. Definition of the Multipole Moments and of the Density Splits

2.1. Definition of the Moments

The moments of a charge distribution with respect to any center \mathbf{x}^0 over a domain D are defined as:

$$M(\rho, \mathbf{x}^0, n, \{e_i\}) = \int_D \sum_{k=1}^3 (x_k - x_k^0)^{n_k} \rho(\mathbf{x}) d\mathbf{x}, \quad (3a)$$

$$\{e_i\}: \text{ the set of orthonormal basis vectors,} \quad (3b)$$

$$\mathbf{n} = \langle n_1, n_2, n_3 \rangle, n_i \text{ a non-negative integer.} \quad (3c)$$

The charge density is assumed to be given by:

$$\rho(\mathbf{x}) = \sum_{i=1}^{n_o} \text{Fr}_i \phi_i^2(\mathbf{x}), \quad (4a)$$

$$\phi_i(\mathbf{x}) = \sum_{j=1}^{n_b} c_{ij} B_j(\mathbf{x}), \quad (4b)$$

$$n_o: \text{ number of molecular orbitals,} \quad (4c)$$

$$n_b: \text{ number of basis functions,} \quad (4d)$$

$$\text{Fr}_i: \text{ fractional occupancy of the } i\text{th MO, } 0 \leq \text{Fr}_i \leq 2, \quad (4e)$$

$$B_j(\mathbf{x}): j\text{th basis function,} \quad (4f)$$

$$c_{ij}: \text{ constants.} \quad (4g)$$

Let

$$\mathbf{x}^j = (x_1^j, x_2^j, x_3^j): \text{ center of the } j\text{th basis function.} \quad (5a)$$

The set $\{\mathbf{x}^j\}$ is contracted into a 1-1 sequence

$$r(i), \quad i = 1, \dots, n_c. \quad (5b)$$

Each $\phi_i(\mathbf{x})$ must be rewritten as a sum over linear combinations of subsets of the basis functions which have the same centers:

$$C(k) \equiv \{B_j(\mathbf{x}) \mid \mathbf{x}^j = r(k)\}, \quad (6a)$$

$$\phi_i(\mathbf{x}) = \sum_{k=1}^{n_c} \psi_i(k, \mathbf{x}), \quad (6b)$$

$$\psi_i(k, \mathbf{x}) = \sum_{B_j(\mathbf{x}) \in C(k)} c_{ij} B_j(\mathbf{x}). \quad (6c)$$

Two basic alternatives for the assignment of two-center densities to the $d(k, \mathbf{x})$ have been used. 1) The first was a convenient generalization of the Mulliken split used by Rein [6]. It allows the assignment of the overlap density to a third center, which will be shown to have great advantages. It is described as follows:

$$d(k, \mathbf{x}) = \sum_{i=1}^{n_o} \text{Fr}_i [\psi_i^2(k, \mathbf{x}) + \sum_{p=q+1}^{n_c} \sum_{q=1}^{n_c} S(k, p, q) \psi_i(p, \mathbf{x}) \psi_i(q, \mathbf{x})], \quad (7a)$$

$$S(k, p, q): \text{ parameters defining the split of the density,} \quad (7b)$$

$$\sum_{k=1}^{n_c} S(k, p, q) = 2. \quad (7c)$$

2) The second alternative was investigated to determine whether a decrease in the range of the overlap density despite the concomitant increase in the asymmetry of the $d(k, \mathbf{x})$ could increase the accuracy of lower-order approximations. It can be described as follows. Consider a plane perpendicular to

$$u = (r(q) - r(p)) / |r(q) - r(p)| \quad (8a)$$

and passing through the point

$$r_o(p, q) = (w(q)r(p) + w(p)r(q)) / (w(p) + w(q)), \quad (8b)$$

$$w(p), (p = 1, \dots, n_c): \text{ positive input parameters.} \quad (8c)$$

Let

$$\chi(p, q, \mathbf{x}) = \begin{cases} 1 & \text{if } \mathbf{u} \cdot (\mathbf{x} - \mathbf{r}_0(p, q)) < 0 \\ 0 & \text{otherwise.} \end{cases} \quad (8d)$$

Then

$$d(k, \mathbf{x}) = \sum_{i=1}^{n_o} \text{Fr}_i[\psi_i^2(k, \mathbf{x})] + \sum_{p=1}^{n_c} \sum_{q=1}^{n_c} \chi(p, q, \mathbf{x}) \psi_i(p, \mathbf{x}) \psi_i(q, \mathbf{x}). \quad (9)$$

2.2. Specification of the Multipole Expansions Used

Results from two choices made for splits of type (1) will be discussed. The first, proposed by Mulliken and considered by Rein [6] is defined by

$$S(k, p, q) = \delta_{pk} + \delta_{qk}. \quad (10)$$

It will be called the Mulliken split. The second removes all overlap density from a selected set of centers and will be called a "very extreme split". It has an immediate advantage based on the following consideration. For any of the conventional basis sets, after all overlap densities have been excluded what remains in $d(k, \mathbf{x})$ is a linear combination of functions of the form:

$$f(|\mathbf{x}|)H(\mathbf{x}), \quad (11a)$$

$$H(\mathbf{x}): \text{ a surface spherical harmonic of order } \leq 2n \text{ (in the sense defined by Hobson [9a]) about the center } \mathbf{x}^k, \quad (11b)$$

$$n: \text{ the highest order of spherical harmonics involved in the functions of } C(k). \quad (11c)$$

After integration over $|\mathbf{x}|$ this implies that the set is exactly represented by a sum of spherical harmonics of order $\leq 2n$ [9b]. In our calculations using a very extreme split, all overlap densities have been transferred to the oxygen atom of the water molecule. This minimizes the number of interactions involved in the split calculations.

The second split alternative will be called a "sharp split" and is defined by

$$w(k) = 1, \quad k = 1, \dots, n_c, \quad (12)$$

i.e., the plane dividing the overlap density between any two centers p and q contains the midpoint of $\mathbf{r}(p) - \mathbf{r}(q)$.

Finally, for the case of the single center expansion, calculations for different choices of \mathbf{x}^0 in the neighborhood of the O nucleus were made over distances *ca.* 10% of the O-O distance. These had no marked influence and all results referring to one-center expansion are for the oxygen nucleus as the \mathbf{x}^0 .

3. Comparison of the Different Multipole Techniques

3.1. Accuracy as a Function of Multipole Order and Expansion Type

The limiting value for the energy E for a given orientation was estimated as follows:

1) The expansion type presumed to yield the greatest accuracy was inferred from inspection of the increments $[E(n) - E(n-1)]$. 2) $E(n)$ for the highest order (i.e., $n = 10$ in this study) for this type was adopted as the estimate.

Table 1. The error in the interaction energies $E(n)$ of expansions of different types in perpendicular orientations. 1) The distance of the oxygens, $R(\text{O-O})$ is in Å. 2) The angle θ is in degrees and is defined in Sect. 3.1. 3) The entries in parentheses are the last relative increments $|1 - [E(9)/E(10)]|$ for the type of expansion chosen for inferring an approximation to the limiting E (cf. Sect. 3.1). 4) All other entries are the errors of the particular approximation: $|1 - E(n)/E(\text{limit})|$ (cf. Sect. 3.1). 5) The number after E is the corresponding power of ten; thus, $.13E - 1 = .013$. 6) All interactions of order $n' \leq n$ are included in $E(n)$

Expansion Type	θ	$R(\text{O-O})$	n			
			4	6	8	10
Molecular	0.0	3.0	.13E - 1	.15E - 1	.18E - 2	.39E - 3
Very extreme split	0.0	3.0	.52E - 2	.45E - 3	.13E - 3	(.35E - 4)
Mulliken split	0.0	3.0	.57E - 2	.26E - 1	.19E - 1	.84E - 2
Sharp split	0.0	3.0	.25E - 1	.11E - 1	.17E - 3	.12E - 1
Molecular	60.0	3.0	.93E - 1	.33E - 1	.82E - 2	.85E - 3
Very extreme split	60.0	3.0	.50E - 1	.46E - 2	.50E - 3	(.93E - 4)
Mulliken split	60.0	3.0	.58E - 1	.23E - 1	.67E - 2	.18E - 2
Sharp split	60.0	3.0	.68E - 2	.11E - 1	.28E - 1	.70E - 1
Molecular	120.0	3.0	.14E + 1	.27E + 0	.24E + 0	.77E - 1
Very extreme split	120.0	3.0	.75E + 0	.39E - 1	.12E - 1	(.28E - 2)
Mulliken split	120.0	3.0	.70E + 0	.76E - 1	.35E + 0	.32E + 0
Sharp split	120.0	3.0	.64E - 1	.15E + 0	.15E + 0	.84E - 1
Molecular	180.0	3.0	.35E + 0	.19E + 0	.34E - 1	.94E - 2
Very extreme split	180.0	3.0	.52E - 3	.30E - 1	.27E - 2	(.37E - 3)
Mulliken split	180.0	3.0	.10E + 0	.69E - 3	.47E - 1	.17E + 0
Sharp split	180.0	3.0	.33E - 1	.18E - 1	.67E + 0	.83E + 0
Molecular	0.0	2.72	.22E - 1	.22E - 1	.35E - 2	.79E - 3
Very extreme split	0.0	2.72	.10E - 1	.79E - 3	.14E - 3	(.81E - 4)
Mulliken split	0.0	2.72	.58E - 3	.51E - 1	.52E - 1	.30E - 1
Molecular split	60.0	2.72	.12E + 0	.49E - 1	.15E - 1	.19E - 2
Very extreme split	60.0	2.72	.69E - 1	.58E - 2	.96E - 3	(.13E - 3)
Mulliken split	60.0	2.72	.87E - 1	.42E - 1	.17E - 1	.62E - 2
Molecular	120.0	2.72	.16E + 1	.80E - 1	.12E + 0	.42E - 1
Very extreme split	120.0	2.72	.31E + 0	.52E - 2	.60E - 2	(.13E - 2)
Mulliken split	120.0	2.72	.31E + 0	.48E - 1	.36E + 0	.11E + 0
Molecular	180.0	2.72	.63E + 0	.37E + 0	.67E - 1	.35E - 1
Very extreme split	180.0	2.72	.36E - 2	.62E - 1	.57E - 2	(.58E - 3)
Mulliken split	180.0	2.72	.43E - 1	.19E + 0	.28E + 0	.76E - 1

Two types of orientations were considered. *Type 1 (perpendicular)*: Let D and A denote donor and acceptor molecules, respectively. The donor H_D is on the O_D-O_A line. Let b_A, b_D be the bond angle bisectors for A and D pointing toward the hydrogens. Let u lie in the donor plane and be either of the two normals to the O_D-O_A line. The two molecular planes are perpendicular. The angle θ between b_A and $(O_D \rightarrow O_A)$ is positive if $(b_A \cdot u)$ and $(b_D \cdot u)$ are of opposite sign. *Type 2 (stacked)*: The O-O line is perpendicular to the two molecular planes and γ is an angle between the bisector of molecule 1 and the projection of the bisector of molecule 2 on the plane of the first. Representative results¹ are presented in Tables 1-2.

Table 2. The error in the interaction energies $E(n)$ of expansions of different types in stacked orientations. 1) The angle γ is in degrees and is defined in Sect. 3.1. 2) For further explanation, see the legend of Table 1

Expansion Type	γ	$R(O-O)$	n			
			4	6	8	10
Molecular	0.0	3.0	.96E - 1	.25E - 1	.65E - 2	.12E - 2
Very extreme split	0.0	3.0	.11E - 1	.11E - 2	.23E - 3	.24E - 3
Mulliken split	0.0	3.0	.19E - 1	.69E - 3	.69E - 3	.23E - 3
Sharp split	0.0	3.0	.69E - 2	.56E - 3	.66E - 4	(.47E - 5)
Molecular	180.0	3.0	.34E + 1	.13E + 1	.55E + 0	.23E + 0
Very extreme split	180.0	3.0	.23E + 0	.84E - 1	.20E - 1	.46E - 3
Mulliken split	180.0	3.0	.24E + 0	.18E - 1	.20E - 2	.37E - 2
Sharp split	180.0	3.0	.82E - 1	.24E - 2	.27E - 2	(.24E - 2)

The results of Tables 1-2 show that: 1) in general the accuracy advantage of the split decreases sharply with the accuracy sought and, therefore, with the order of the approximation used; 2) in these calculations on small H-bonded molecules, the very extreme split gives the highest accuracy in orientations of greatest interest and in all cases its accuracy is at least comparable to the best; 3) the Mulliken split gave significantly lower accuracy than the very extreme and was in many cases outperformed by the molecular expansion at higher orders; 4) the sharp split showed greater accuracy at orientations of lesser interest.

Finally, calculations at over 200 orientations and distances using the wave function of Popkie, Kistenmacher and Clementi [10] confirmed the general superiority of the very extreme split over the molecular expansion.

3.2. Time Requirements of the Different Types of Expansions

Data on the time requirements for different types of expansions are presented in Table 3. Although the number of multipole series calculations required for the total energy is

¹ The wave function was provided by Diercksen and Kraemer in a private communication involving slight variations in the basis set published in [1].

Table 3. Time requirements (sec) for computing the interaction energy with different types of expansions

Expansion Type	<i>n</i>					
	4	6	8	10	12	14
Molecular	0.097	0.133	0.229	0.430	0.664	1.29
Any split, other than the very extreme	0.148	0.407	1.10	2.70	5.1 ^a	12. ^a
Very extreme split	0.098	0.179	0.376	0.908	1.53	3.07

^a Estimated.

proportional to $(N_1 N_2)$, the product of the number of distributions used for the two interacting systems, inspection of the times listed in Table 3 shows that at lower orders there is a substantial contribution from initialization common to all centers. Furthermore, a comparison of times for the very extreme and other splits in Table 3 shows the marked savings which arise from the vanishing of higher order moments for centers devoid of overlap density.

4. Considerations for the Choice of Expansion Type and Order

The following points should be considered in the selection of the compromise between an increase in the order of the multipole series and an increase in the number of distributions into which the molecular density is partitioned. 1) It is reasonable to extrapolate from our calculations on $H_2O \dots H_2O$ to the case where interactions between AH_x of one molecule with atom B of another ($R-AH_x \dots B-R'$) make significant contributions to the total energy. In such a case, it is expected that a very extreme split with a transfer of all overlap densities involving the H's to A will yield a similar accuracy advantage to that found in water. It seems plausible that for ($R-A-C \dots B-R'$) it would likewise be advantageous to use a very extreme split with all overlap involving C transferred to A. 2) The results on stacked orientations suggest that for less directly interacting centers the very extreme split will probably lose its accuracy advantage in comparison with other splits. 3) Although the additional accuracy gained by a split is in general expected to increase with the size of interacting systems, the aforementioned asymptotic increase in time makes it imperative to group the nuclei into subsets with a common expansion center. 4) The very extreme split with its advantage of limiting harmonic types can be applied usefully only to centers within a "reactive" group. For other groups another split type is required. One can expect that there will be a maximum number of groups from the standpoint of accuracy as well as from time economy on the basis of the following two observations: (a) there were certain orientations for which either the Mulliken or the sharp split gave results which were no better than those of a single center expansion, and others for which they were worse; (b) in most cases these splits were more accurate at lower orders only. 5) For the small system tested, at orientations and distances of greatest physical interest an increase of between two and four orders yielded an accuracy for the

one-center expansion approximately equal to that of the best multipole decomposition, i.e., the very extreme split. 6) A split moment program is somewhat more complex. 7) The use of split moments in calculations on crystals may sacrifice symmetry elements that might be present for the appropriate choice of a single molecular center.

Appendix A

Specification of the Moment Computation Program

The CDC 6600 Fortran program MOMENTS, available on request, computes the moments of a charge distribution, subject to the following restrictions:

1) An input parameter, N_{\max} , determines that the moments will be given for all orders $N = n_1 + n_2 + n_3$ such that

$$N \leq N_{\max} \leq 14 \quad (\text{A1})$$

2) Each basis function $B_j(x)$ is assumed to be a contracted normalized linear combination of normalized Gaussians of the form:

$$B_j(x) = N_j \left[\sum_{\{m\}} a_m^j \prod_{p=1}^3 (x_p - x_p^j)^{m_p} \right] \sum_{q=1}^{n_j} N_q^j b_q^j \exp[-\alpha_q^j |x - x^j|], \quad (\text{A2a})$$

$$\{m|m_k \text{ is a non-negative integer and } m_1 + m_2 + m_3 \leq 3\}, \quad (\text{A2b})$$

$$a_m^j, b_q^j, \alpha_q^j: \text{ parameters; } N_j, N_q^j: \text{ normalization constants, } \quad (\text{A2c})$$

$$n_j: \text{ number of Gaussians contracted in the } j\text{th basis function.} \quad (\text{A2d})$$

3) The input syntax is compatible with the POLYATOM system of programs [12].

Appendix B

Algorithms, Storage and Timing for the Moment Calculation

1) Substitution of the expression for the density, Eqs. (4, 5, A2) into the definition of the moments, Eq. (3), yields linear combinations of product of integrals that are of the following form:

$$\int_{-\infty}^{\infty} (x - x_k)^{n_k} (x - x_p)^{n_p} (x - x_q)^{n_q} \exp[-\alpha_p(x - x_p)^2] \exp[-\alpha_q(x - x_q)^2] dx \quad (\text{B1})$$

The product of the two Gaussians is replaced by a single Gaussian through the standard transformation of perfect squares:

$$-\alpha_p(x - x_p)^2 - \alpha_q(x - x_q)^2 = [-\alpha_p\alpha_q(x_p - x_q)^2/\alpha_{pq}] - \alpha_{pq}(x - x_{pq})^2, \quad (\text{B2a})$$

$$x_{pq} = (\alpha_p x_p + \alpha_q x_q)/\alpha_{pq}; \quad \alpha_{pq} = \alpha_p + \alpha_q. \quad (\text{B2b})$$

Since, in general, for each pair of basis functions the maximum possible number of different moments is much greater than the maximum number of coefficients in the product harmonic, it is advantageous to express the integral (B1) as a linear combination

of integrals of the following form:

$$\int_{-\infty}^{\infty} (x - x_k)^{m_k} \exp[-\alpha_{pq}(x - x_{pq})^2] dx, \quad (\text{B3a})$$

$$x_k: \text{center coordinate for moment expansion.} \quad (\text{B3b})$$

This integral can be evaluated either by applying the transformation $\eta = x - x_k$ or the transformation $\eta' = x - x_{pq}$, leading to integrals of the form:

$$\int_{-\infty}^{\infty} \eta^{m_k} \exp[-\alpha_{pq}(\eta - (x_{pq} - x_k))^2] d\eta, \quad (\text{B4})$$

or

$$\int_{-\infty}^{\infty} (\eta' - (x_k - x_{pq}))^{m_k} \exp[-\alpha_{pq}\eta'^2] d\eta', \quad (\text{B5})$$

respectively. The integral (B4) can be evaluated recursively,

$$\begin{aligned} \int_{-\infty}^{\infty} x^{L+2} \exp[-\alpha(x-r)^2] dx &= [(L+1)/2\alpha] \int_{-\infty}^{\infty} x^L \exp[-\alpha(x-r)^2] dx \\ &+ r \int_{-\infty}^{\infty} x^{L+1} \exp[-\alpha(x-r)^2] dx, \end{aligned} \quad (\text{B6})$$

while the integral (B5) can be evaluated through the binomial expansion. Since the number of operations is less for the recursion whenever $m_k \geq 5$ and test calculations on a wide range of parameters have shown no propagation of round-off errors, the form (B4) was used throughout the program.

2) The calculation for the split by perpendicular planes is done similarly, with the following two modifications: a) for each pair of centers a rotation of coordinates is needed to make \mathbf{u} of Eq. (8a) one of the basis vectors; b) the recursion for the coordinate x corresponding to \mathbf{u} is modified as follows. The first step evaluated the incomplete error function and is continued as:

$$\begin{aligned} \int_A^B x^{L+2} \exp[-\alpha(x-r)^2] dx &= [(L+1)/2\alpha] \int_A^B x^L \exp[-\alpha(x-r)^2] dx \\ &+ r \int_A^B x^{L+1} \exp[-\alpha(x-r)^2] dx - B^{L+1} \exp[-\alpha(B-r)^2]/2\alpha \\ &+ A^{L+1} \exp[-\alpha(A-r)^2]/2\alpha. \end{aligned} \quad (\text{B7})$$

3) The coefficients of the polynomials in three variables as well as the different moments are stored in linear arrays in: a) blocks of increasing $N = n_1 + n_2 + n_3$; b) within each block of N in blocks of increasing n_3 ; c) within each block of n_3 in blocks of increasing n_2 . The address of the coefficient belonging to the term with exponents (n_1, n_2, n_3) is:

$$[N(N(N+3)+2)/6] + [n_3(2N-n_3+3)/2] + n_2 + 1. \quad (\text{B8})$$

Note that the term $N(N(N+3)+2)/6$ gives the number of coefficients in a polynomial in x_1, x_2, x_3 of order $(N-1)$.

4) The times required to compute various moments from wave functions of different size are given in Table 4.

Table 4. Time requirements (sec) of the moment computation using different basis sets

Molecule	No. of Basis Functions	No. of Gaussians	N_{\max}				
			3	5	6	10	14
H ₂ O ^a [11]	14	33		14			163
H ₂ O ^b [11]	14	33		9			105
H ₂ O ^c [11]	14	33		16			173
H ₂ O ^c [1, 2]	35	56	24	49		243	
H ₂ O ^d [1, 2]	35	56		32		~155	
H ₂ O ^e [1, 2]	35	56			105	371	
(H ₂ O) ₂ ^c [1, 2]	70	112				1247	
H ₂ O ^c [10]	29	56				256	594
H ₂ O ^d [10]	29	56					313

^a Molecular (H centered);
split;

^b Molecular (O centered);

^c Mulliken split;

^d Very extreme

^e Sharp split.

Appendix C

Transformation of the Moments

A tested CDC 6600 Fortran program called MOMTRSF is also available on request. It is compatible in its input with the program MOMENTS and can perform the following transformations: 1) Contraction of the moments. Consider any set of centers \mathbf{x}^k , $1 \leq k \leq n'_c$, and the corresponding sets of moments $\{M^k(\rho^k, \mathbf{x}^k, \mathbf{n}, \{e_i\}) | n_1 + n_2 + n_3 \leq N_{\max}\}$. Choose $\mathbf{x}^0 = \mathbf{x}^j$, $1 \leq j \leq n'_c$. The moments $\{M(\rho, \mathbf{x}^0, \mathbf{n}, \{e_i\})\}$ of

$$\rho = \sum_{k=1}^{n'_c} \rho^k$$

are generated. 2) Translation of the center of expansion. The set of moments $\{M(\rho, \mathbf{x}^0, \mathbf{n}, \{e_i\})\}$ is converted to the set of moments $\{M'(\rho, \mathbf{x}^{0'}, \mathbf{n}, \{e_i\})\}$ referring to another center $\mathbf{x}^{0'}$. 3) Rotation of the coordinate system around the center of expansion. The set of moments $\{M(\rho, \mathbf{x}^0, \mathbf{n}, \{e_i\})\}$ is converted to the set of moments $\{M''(\rho, \mathbf{x}^0, \mathbf{n}, \{e'_i\})\}$, where $\{e'_i\}$ is the set of orthonormal basis vectors of the rotated system.

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