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Polarized basis sets and the calculation of infrared intensities from nuclear electric shielding tensors

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The idea of the basis set polarization which follows from the known dependence of basis set functions on the perturbation strength is applied to the calculation of the dipole moment derivatives with respect to nuclear displacements. The differentiation of the dipole moment function is replaced by the straightforward evaluation of derivatives of the intramolecular electric field with respect to the external electric field strength. The method and its efficiency are illustrated by a series of calculations of the dipole moment derivatives for the water molecule. Already a polarized basis set of 26 CGTO's derived from the minimal CGTO basis set provides fairly reasonable results.

Key words: Basis sets — Perturbation-dependent basis sets — Polarized basis sets — Hellmann-Feynman theorem — Infrared intensities — Molecular properties — H_2O

1. Introduction

The band intensities in infrared spectra of polyatomic molecules provide a highly sensitive probe of the molecular electronic structure. Owing to recent advances in experimental techniques there is an increasing interest in accurate theoretical methods for the determination of the corresponding data [1].

The calculation of the infrared band intensity can in principle be reduced to the evaluation of derivatives of the molecular dipole moment with respect to nuclear displacements [2]. Different computational techniques have been developed for that purpose over the past years. Early calculations have mostly been based on

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the straightforward numerical evaluation of the dipole moment derivatives [3]. A partly analytic technique has been suggested by Komornicki and McIver [4] and more recently exploited by Bacskay et al. [5].

The major bottleneck of the above-mentioned methods is either the number of independent calculations at different molecular geometries [3] or a rather time-consuming evaluation of molecular gradients [4–6]. Since the dipole moment derivative is a second-order molecular property [7], it is obvious that its accurate calculation must be carried out with sufficiently large basis sets. The number of numerical evaluations of derivatives is certainly minimized in the methods based on gradient techniques [4, 5]. However, the evaluation of gradients of all molecular integrals makes such calculations with appropriately extended basis sets prohibitively time-consuming.

Recently, Lazzeretti and Zanasi [8] suggested the evaluation of the dipole moment derivatives from the nuclear electric shielding tensors in molecules. Since the nuclear shielding can be alternatively expressed in terms of the derivatives of the intramolecular electric field at the given nucleus with respect to the external electric field, the corresponding finite-field technique would offer similar advantages to those of the gradient method. As a matter of fact both techniques are closely related and become identical in the complete basis set limit. This indicates that the suggestion of Lazzeretti and Zanasi might be useful only in large basis set calculations. Indeed, quite encouraging results have been obtained for basis sets [9, 10] much larger than those commonly employed in molecular calculations.

In the present paper we want to propose an alternative computational scheme for the evaluation of the dipole moment derivatives which is based on the numerical evaluation of the derivatives of the intramolecular electric fields with respect to the external electric field and simultaneously avoids the calculation of gradients of molecular integrals. The proposed scheme is based on a specific extension of the atomic basis set and follows from the concept of polarized basis sets which has recently been exploited in accurate calculations of molecular dipole moments [11]. The method presented in this paper is devised for calculations of the molecular dipole moment derivatives with relatively standard, highly contracted basis sets, e.g. of double-zeta quality. The basis set polarization due to virtual nuclear displacements is determined by the known dependence of basis set functions on nuclear positions. The same also applies to the contraction coefficients for polarization functions derived by polarizing the given initial basis set of contracted Gaussian orbitals.

The efficiency of the computational method proposed in this paper is illustrated by calculations of the dipole moment derivatives for the water molecule with GTO/CGTO basis sets of different quality. The theoretical background of the method is briefly surveyed in the next section. In Sect. 3 the applicability of the relation between the dipole moment derivatives and the nuclear shielding tensor is illustrated and discussed. A general discussion of the method and conclusions are presented in Sect. 4.

2. The nuclear electric shielding in molecules and its relation to the dipole moment derivatives

The theory of nuclear electric shielding in molecules has recently been given a comprehensive discussion by Lazzeretti and Zanasi [8, 10] and represents an alternative formulation of what is known as the polar tensor method [1, 2, 12, 13]. For the purpose of summarizing the basic formulae necessary for the present discussion, let us consider the electronic Hamiltonian H of a vibrating molecule embedded in a homogeneous static electric field $\underline{F}$. Through the first order in nuclear displacements $\underline{X}_A$ the Hamiltonian can be written as:

$$H(\underline{X}, \underline{F}) = H(0, 0) + \sum_A \left(\frac{\partial H}{\partial X_{A\beta}} \right) X_{A\beta} + F_\alpha \cdot m^0_\alpha + F_\alpha \sum_A Z_A X_{A\alpha}, \tag{1}$$

where m^0_α is the αth component of the molecular dipole moment at the reference nuclear configuration. The summation over repeated Greek indices is implicit. In order to stress the double perturbation character of the problem the Hamiltonian (1) is rewritten as:

$$H(\underline{X}, \underline{F}) = H^0 + \sum_A H^{10}_{A\beta} X_{A\beta} + H^{01}_\alpha F_\alpha + F_\alpha \sum_A H^{11}_{\alpha,A\beta} X_{A\beta} \tag{2}$$

where $H^0 = H(0, 0)$ is the electronic Hamiltonian for the reference nuclear geometry in the absence of the external field and

$$H^{10}_{A\beta} = \left(\frac{\partial H}{\partial X_{A\beta}} \right)_0 = -Z_A \sum_i \frac{x_{i\beta} - X^0_{A\beta}}{|\underline{x}_i - \underline{X}^0_A|^3} - Z_A \sum_{B \neq A} \frac{X^0_{B\beta} - X^0_{A\beta}}{|\underline{X}^0_B - \underline{X}^0_A|^3} \tag{3a}$$

$$H^{01}_\alpha = m^0_\alpha = \sum_A Z_A X^0_{A\alpha} - \sum_i x_{i\alpha}, \tag{3b}$$

The summation over i corresponds to all electrons and $x_{i\alpha}$ is the αth component of the ith electron coordinate while $X^0_{A\alpha}$ denotes the αth component of the equilibrium position vector of the nucleus A.

In the double perturbation expansion of the total energy

$$E(\underline{X}, \underline{F}) = E^0 + \sum_A X_{A\beta} E^{10}_{A\beta} + F_\alpha E^{01}_\alpha + \sum_A F_\alpha X_{A\beta} E^{11}_{\alpha,A\beta} + \cdots \tag{4}$$

the quantitity of interest, $E^{11}_{\alpha,A\beta}$, is given by

$$E^{11}_{\alpha,A\beta} = Z_A \delta_{\alpha\beta} + \langle \Psi^0 | H^{10}_{A\beta} | \Psi^{01}_\alpha \rangle + \langle \Psi^0 | H^{01}_\alpha | \Psi^{10}_{A\beta} \rangle$$

where Ψ^0, Ψ^{01}_α, and $\Psi^{10}_{A\beta}$ denote the unperturbed wave function and the solutions of the corresponding first-order perturbed equations, respectively. If the solution of the electronic Schrödinger equation with respect to the relevant perturbation parameters satisfies the Hellmann-Feynman theorem [14], the following two alternative formulae for $E^{11}_{\alpha,A\beta}$:

$$E^{11}_{\alpha,A\beta} = Z_A \delta_{\alpha\beta} + \left\{ \frac{\partial}{\partial F_\alpha} \langle \Psi(\underline{F}) | H^{10}_{A\beta} | \Psi(\underline{F}) \rangle \right\}_{F=0} \tag{5a}$$

and

$$E^{11}_{\alpha,A\beta}=\left\{\frac{\partial}{\partial X_{A\beta}}\langle\Psi(\underline{X})|H^{01}_{\alpha}|\Psi(\underline{X})\rangle\right\}_{\underline{X}=\underline{X}^{0}}, \tag{5b}$$

are equivalent by virtue of the interchange theorem [15] and it follows from the definition of perturbation operators that $E^{11}_{\alpha,A\beta}$ is the derivative of the αth component of the molecular dipole moment with respect to the βth component of the cartesian displacement of the nucleus A, $\frac{\partial\mu_\alpha}{\partial X_{A\beta}}$.

According to the definition of the nuclear electric shielding tensor $\gamma_{\alpha,A\beta}$ for the nucleus A [10]

$$\gamma_{\alpha,A\beta}=-2\langle\Psi^{0}|\frac{1}{Z_A}H^{10}_{A\beta}|\Psi^{01}_{\alpha}\rangle \tag{6}$$

one can write [9, 11]

$$\frac{\partial\mu_\alpha}{\partial X_{A\beta}}=Z_A(\delta_{\alpha\beta}-\gamma_{\alpha,A\beta})=P_{\alpha,A\beta} \tag{7}$$

where $P_{\alpha,A\beta}$ is the polar tensor of the nucleus A [1, 2, 12, 13]. The importance of Eq. (7) follows from the fact that the evaluation of $\gamma_{\alpha A\beta}$ can be made computationally much easier and more efficient than the calculation of $P_{\alpha,A\beta}$ from the induced dipole moments (5b). For a system with N nonequivalent nuclei, using Eq. (5b) directly would mean the computation of $3N$ derivatives, while all elements of $\gamma_{\alpha,A\beta}$ can be obtained from three derivatives of the matrix element

$$\langle\Psi(\underline{F})|\frac{1}{Z_A}H^{10}_{A\beta}|\Psi(\underline{F})\rangle, \tag{8}$$

i.e. from the average values of the intramolecular electric field calculated in the presence of some external electric field $\underline{F}$. However, as already mentioned, the advantages of this observation can only be exploited if $\Psi(\underline{X},\underline{F})$ satisfies the Hellmann-Feynman theorem with respect to the nuclear displacement perturbation. In general, the equivalence of three different definitions of the dipole moment derivative with respect to nuclear displacements:

$$M^{(1)}_{\alpha,A\beta}=\frac{\partial^2}{\partial F_\alpha\partial X_{A\beta}}E(\underline{X},\underline{F}), \tag{9a}$$

$$M^{(2)}_{\alpha,A\beta}=\frac{\partial}{\partial X_{A\beta}}m_\alpha(\underline{X}), \tag{9b}$$

and

$$M^{(3)}_{\alpha,A\beta}=Z_A\left\{\frac{\partial}{\partial F_\alpha}\varepsilon_{A\beta}(\underline{F})+\delta_{\alpha\beta}\right\}, \tag{9c}$$

where $m_\alpha(\underline{X})$ is the average value of the αth component of the molecular dipole moment at the geometry $\underline{X}$ and $\varepsilon_{A\beta}(\underline{F})$ is the βth component of the average value of the intramolecular electric field at the nucleus A in the external electric field $\underline{F}$, is achieved only if $\Psi(\underline{X}, \underline{F})$ satisfies the Hellmann–Feynman theorem with respect to both $\underline{X}$ and $\underline{F}$.

However, for a number of molecular wave functions [6, 16–19] the appropriate form of the Hellmann–Feynman theorem is not satisfied, i.e.,

$$\varepsilon_{A\beta}(\underline{F}) \neq \frac{1}{Z_A} \frac{\partial}{\partial X_{A\beta}} E(\underline{X}, \underline{F}) - \delta_{\alpha\beta}, \tag{10a}$$

and/or

$$m_\alpha(\underline{X}) \neq \frac{\partial}{\partial F_\alpha} E(\underline{X}, \underline{F}), \tag{10b}$$

and thus the equivalence between the three definitions (9) must be considered with a particular caution.

In this context the sum rule [8, 9, 20]:

$$\sum_A Z_A \gamma_{k,Ak} = n, \tag{11}$$

where n is the number of electrons, or an equivalent condition for the diagonal components of the polar tensor [1, 2]:

$$\sum_A P_{k,Ak} = 0, \tag{12}$$

become of particular interest. For the dipole moment derivatives calculated from the explicit geometry dependence of $m_\alpha(\underline{X})$ the sum rule (12) will be satisfied provided $m_\alpha(\underline{X}) = (\partial/\partial F_\alpha)\, E(\underline{X}, \underline{F})$. The conditions for the validity of the latter equivalence have been discussed previously [17–19]. In the SCF HF approximation, which will be considered in this paper, the equivalence of both sides of Eq. (10b) is ensured if the basis sets do not depend explicitly on the external electric field strength [17, 18]. This condition is met by the majority of SCF HF calculations, and thus, the validity of (12) is quite obvious.

To satisfy the sum rule (11) one needs to require the equivalence of both sides of Eq. (10a). However, most basis sets currently employed in molecular calculations inherently depend on the positions of the nuclei. This obviously results in differences between the Hellmann–Feynman term (the l.h.s. of Eq. (10a)) and the derivative definition on the r.h.s. of Eq. (10a) [4–6]. Hence, the evaluation of the l.h.s. of Eq. (11) provides a useful check on the quality of the given wave function. Checking the sum rule for the nuclear shielding tensor will qualify the validity of calculations of $P_{\alpha,A\beta}$ with the aid of a much simpler method based on Eq. (9c). On the other hand, the non-equivalence of both sides of Eq. (10a) may suggest convenient ways of improving the wave function [11].

3. Evaluation of the dipole moment derivatives from nuclear shielding factors. Polarized GTO/CGTO basis sets

The calculations reported in this paper are limited to the SCF HF approximation. Extending this study to a correlated level of approximation is not expected to contribute any considerable novelty since the major problem is concerned with the basis set dependence on nuclear displacements. The water molecule has been chosen as an illustrative example and all calculations correspond to its experimental equilibrium geometry ($O[0.0, 0.0, 0.0], H_1, H_2[0.0, \pm 1.43153, 1.10941]$ a.u.). However, both the geometry derivatives of the dipole moment and the electric field derivatives of the intramolecular electric fields have been computed numerically from the pointwise $m_\alpha(\underline{X})$ and $\varepsilon_{A\beta}(\underline{F})$ curves. Different values of the nuclear position shifts and electric fields have been explored in order to guarantee the appropriate numerical accuracy. It is perhaps worthwhile to mention that the numerical differentiation of $\varepsilon_{A\beta}(\underline{F})$ with respect to F_α is far more stable than the numerical differentiation of $m_\alpha(\underline{X})$ with respect to $X_{A\beta}$.

The first step in our present study was to evaluate the degree of the violation of the sum rule (11) for a series of different GTO/CGTO basis sets with *d* and *f* functions on oxygen and *p* and *d* functions on hydrogens [9]. The following five GTO/CGTO basis sets have been employed:

A: $O[7.3/2.1], H[4/1]$
Taken from Ref. [21] (for *O*) and Ref. [22] (for *H*)

B: $O[10.5/4.2], H[4/2]$
Double-zeta set taken from Ref. [23].

C: $O[11.7/5.4], H[6/3]$
Taken from Ref. [24] with contraction coefficients of Salez and Veillard [25] for *O*. The contraction scheme is the same as used in Ref. [26].

D: $O[11.7.1/5.4.1], H[6.1/3.1]$
Basis set *C* extended by the *d*-type function ($\alpha_d = 0.85$) [27] on oxygen and the *p*-type function function ($\alpha_p = 1.0$) on *H*[27].

E: $O[14.8.3.1/9.6.3.1], H[10.2.1/6.2.1]$.
Taken from Ref. [9].

The qualification of these basis sets in terms of the calculated SCF HF energies, dipole moments, the dipole moment derivatives and the sum rules for different components of the nuclear shielding tensor, is given in Table 1. The dipole moment derivatives displayed in this table have been calculated numerically from the dipole moment function. Since all basis sets considered in this paper do not depend on the external electric field strength, the sum rule (12) is satisfied within the limits of numerical accuracy of our calculations.

It follows from the data of Table 1 that fairly reasonable values of the dipole moment derivatives can be calculated with rather poor GTO/CGTO basis sets by the differentiation of the dipole moment curves. This has already been observed

Table 1. Qualification of different GTO/CGTO basis sets for the water molecule with respect to the total energy and molecular properties. All values in a.u.[a]

Property	Basis A	Basis B	Basis C	Basis D	Basis E[b]
E^0	−75.700493	−76.003430	−76.013331	−76.051226	−76.066379
m_z^0	0.9560	1.0557	1.0548	0.8838	0.7831
ε_{Oz}	−0.3533	−0.2481	−0.2064	−0.0801	−0.0048
ε_{H_1y}	0.1697	0.0999	0.0943	0.0079	−0.0072
ε_{H_1z}	0.0774	0.0364	0.0346	−0.0011	−0.0087
$M^{(2)}_{y,Oy}$	−0.295	−0.514	−0.512	−0.549	−0.557
$M^{(2)}_{z,Oz}$	−0.270	−0.385	−0.336	−0.417	−0.429
$M^{(2)}_{y,H_1y}$	0.148	0.257	0.256	0.276	0.278
$M^{(2)}_{y,H_1z}$	−0.219	0.169	−0.170	−0.096	−0.058
$M^{(2)}_{z,H_1y}$	−0.180	−0.102	−0.115	−0.051	−0.060
$M^{(2)}_{z,H_1z}$	0.135	0.200	0.170	0.211	0.214
$\sum_A Z_A \gamma_{y,A_y}$ [c]	2.596	4.680	5.762	7.680	9.756
$\sum_A Z_A \gamma_{z,Az}$ [c]	0.782	2.196	3.188	6.916	9.808

[a] For the geometry and basis set details see text

[b] Numerical calculations with the basis set of Lazzeretti and Zanasi [9]

[c] Evaluated from the numerical derivatives of the intramolecular electric field with respect to the external electric field strength. The exact value is equal to 10

in earlier calculations [3–5] and has significantly contributed to the development of the atomic polar tensor concept [1, 2, 13]. However, how poor the basis sets *A* through *D* are from the point of view of their completeness is indicated by the sums of diagonal components of the electric shielding tensor. Even for a very extended basis set of Lazzeretti and Zanasi [9], the corresponding sum rules are still considerably violated. This violation of the sum rule (11) for the nuclear shielding tensor has, as illustrated by the data of Table 2, even more pronounced effect on the dipole moment derivatives computed according to Eq. (9c). For basis sets *A* through *D* the magnitude of $M^{(3)}_{\alpha,A\beta}$ and even its signs are incorrect.

Hence, the encouraging results of Lazzeretti and Zanasi [8, 9] are primarily due to the use of very large basis sets. The direct extension of the method based on the evaluation of nuclear shielding tensors to larger molecules does not appear to be computationally feasible.

On the other hand the gradient methods advocated by Komornicki et al. and Pulay et al. [4] require the analytic calculations of $3N$ gradients of all molecular integrals. With increasing molecular size and reasonably large basis sets those methods become quite time consuming. An intermediate solution of the dimensionality-timing problem can be achieved by incorporating some elements of the gradient approach in the selection of the basis set.

The success of the gradient method, or equivalently, the numerical differentiation of the dipole moment function (Eq. 9b) follows from the explicit dependence of basis set functions on the perturbation parameter $X_{A\alpha}$. Hence, if the polar tensor

Table 2. Dipole moment derivatives for the water molecule. A comparison of the values obtained from the numerical differentiation of the dipole moment function ($M^{(2)}_{\alpha,A\beta}$, Eq. 9b) with those derived from the components of the nuclear electric shielding tensor ($M^{(3)}_{\alpha,A\beta}$, Eq. 9c). All values in a.u.[a]

	Basis A		Basis B		Basis C		Basis D		Basis E	
$\alpha, A\beta$	Eq. (9b)	Eq. (9c)	Eq. (9b)	Eq. (9c)	Eq. (9b)	Eq. (9c)	Eq. (9b)	Eq. (9c)	Eq. (9b)	Eq. (9c)
y, Oy	−0.295	6.624	−0.514	4.680	−0.512	3.631	−0.549	1.891	−0.557	−0.309
z, Oz	−0.270	8.064	−0.385	6.916	−0.336	5.953	−0.417	2.485	−0.429	−0.259
y, H_1y	0.148	0.390	0.257	0.320	0.256	0.303	0.276	0.316	0.278	0.283
y, H_1z	−0.219	−0.291	−0.169	−0.338	−0.170	−0.323	−0.096	−0.100	−0.058	−0.057
z, H_1y	−0.180	−0.400	−0.102	−0.411	−0.115	−0.405	−0.051	−0.097	−0.060	−0.061
z, H_1z	0.135	0.577	0.200	0.446	0.170	0.430	0.211	0.300	0.214	0.225

[a] See footnotes to Table 1

is calculated according to Eq. (9b), the basis set becomes formally extended by its first-order derivatives with respect to nuclear positions [17], while its actual dimension is the same as for the reference molecular geometry. Hence, by extending the given basis set by the first-order derivatives with respect to $X_{A\alpha}$ one can expect the values of $M^{(2)}_{\alpha,A\beta}$ and $M^{(3)}_{\alpha,A\beta}$ becoming close to each other. This idea of exploiting the inherent dependence of basis set functions on the perturbation strength has recently been used to derive large basis sets for accurate calculations of molecular dipole moments [11]. However, when the initial basis set is relatively uncontracted, the dimension of what is termed the resulting polarized basis set can easily become prohibitively large.

The most important feature of the method devised for the derivation of polarized basis sets is that the differentiation of a CGTO does change its "quantum numbers" as well as the contraction coefficients [11]. The latter are scaled by the appropriate power of orbital exponents of primitive GTO's contributing to the given CGTO. For the initial CGTO, $\chi^{[k]}(\underline{A})$, centered at $\underline{A}$ and characterized "by the set of quantum numbers" $[k]$ with the following expansion in terms of primitive normalized GTO's $g_i^{[k]}(\underline{A}, \alpha_i)$

$$\chi^{[k]}(\underline{A}) = \sum_i c_i g_i^{[k]}(\underline{A}, \alpha_i), \tag{13}$$

where α_i denotes the orbital exponent, the corresponding polarized basis set functions will have the following form

$$\frac{\partial}{\partial X_{A\beta}} \chi^{[k]}(\underline{A}) \sim \{\tilde{\chi}^{[k-1]}(\underline{A}), \tilde{\chi}^{[k+1]}(\underline{A})\}, \tag{14}$$

where

$$\tilde{\chi}^{[k\pm1]}(\underline{A}) = \sum_i c_i' g_i^{[k\pm1]}(\underline{A}, \alpha_i) \tag{15}$$

and

$$c_i' = \sqrt{\alpha_i} \cdot c_i \tag{16}$$

According to the concept of the basis set polarization, both functions resulting from Eq. (14) have to be used to augment the initial basis set. Obviously, this procedure will be of practical value compared to the gradient methods only if the dimension of the original CGTO basis set is relatively small. Hence, the method proposed in the present paper might be convenient for e.g. minimal or double-zeta basis sets. The illustration of its efficiency is given in Tables 3 and 4.

The results recalculated in the present paper for the basis set of Lazzeretti and Zanasi [9] are taken as a reference. It is worth while to mention that the components of the electric shielding tensor computed with Basis E [9] are close to those derived from the experimental data [9, 28] for infrared intensities.

Because of the increase of the size of polarized basis sets compared to the dimension of the initial CGTO set we have also investigated the possibility of

Table 3. Dipole moment derivatives for the water molecule calculated with different polarized basis sets derived from the GTO/CGTO basis sets A and B. The results for polarized basis sets follow from the numerical differentiation of the intramolecular electric field with respect to the external electric field strength (Eq. 9c). All data in a.u.[a]

		Polarized Basis A				Polarized Basis B			
Derivative	Basis A[b]	1[d]	2[e]	3[f]	Basis B[b]	1[d]	2[g]	3[f]	Ref.[b,c]
$M^{(3)}_{y,Oy}$	6.624 (−0.295)	2.384	−0.152	−0.448	4.680 (−0.514)	1.096	1.440	−0.528	−0.309 (−0.557)
$M^{(3)}_{z,Oz}$	8.064 (−0.270)	2.360	−0.016	−0.368	6.916 (−0.385)	1.760	2.080	−0.384	−0.259 (−0.429)
$M^{(3)}_{y,H_1y}$	0.390 (0.148)	0.081	0.090	0.074	0.320 (0.257)	0.267	0.261	0.268	0.283 (0.278)
$M^{(3)}_{y,H_1z}$	−0.291 (−0.219)	−0.051	−0.096	−0.096	−0.338 (−0.169)	−0.077	−0.112	−0.076	−0.057 (−0.058)
$M^{(3)}_{z,H_1y}$	−0.400 (−0.180)	−0.118	−0.113	−0.119	−0.411 (−0.102)	−0.082	−0.128	−0.080	−0.061 (−0.060)
$M^{(3)}_{z,H_1z}$	0.577 (0.135)	0.046	0.052	0.037	0.446 (0.200)	0.212	0.202	0.212	0.225 (0.214)

[a] See footnotes to Table 1

[b] The value in parentheses follows from the numerical differentiation of the dipole moment function according to Eq. (9b)

[c] Reference values calculated with Basis E [9]

[d] Polarized basis set with removed *s* and *p* polarization components on oxygen

[e] Polarized basis set with removed *s* polarization components on oxygen

[f] Complete polarized basis set

[g] Polarized basis set with removed *d* polarization component on oxygen

Table 4. Characterization of different polarized basis sets employed for the calculation of the dipole moment derivatives for the water molecule. All data in a.u.[a]

Property	Basis A	Polarized Basis A[b]			Basis B	Polarized Basis B[c]			Ref.[d]
		1	2	3		1	2	3	
E^0	−75.700493	−75.824999	−75.845986	−75.873749	−76.003430	−76.034858	−76.027087	−76.037212	−76.066379
m_z^0	0.9560	0.7667	0.7796	0.7386	1.0557	0.7961	0.8579	0.7970	0.7831
ε_{Oz}	−0.3533	−0.1090	−0.0185	−0.0074	−0.2481	−0.0724	0.1017	0.0031	−0.0048
ε_{H_1y}	0.1697	0.0393	0.0377	0.0384	0.0999	−0.0046	0.0046	−0.0049	−0.0072
ε_{H_1z}	0.0775	0.0394	0.0370	0.0392	0.0364	−0.0096	−0.0086	−0.0097	−0.0087
$\sum_A Z_A \gamma_{y,Ay}$[e]	2.596	7.454	9.972	10.300	4.680	8.370	8.038	9.992	9.756
$\sum_A Z_A \gamma_{z,Az}$[e]	0.782	7.548	9.912	10.294	2.196	7.816	7.516	9.960	9.808

[a] See footnotes to Table 1

[b] See footnotes d, e, and f to Table 3

[c] See footnotes d, g, and f to Table 3

[d] See footnote c to Table 3

[e] Calculated from the derivatives of $\varepsilon_{A\beta}(\underline{F})$ with respect to F_α

removing some components of polarization functions (15). It can be concluded from the data of Table 3 that the $[k+1]$ component resulting from the given $\chi^{[k]}$ is more important than the component with lowered GTO quantum numbers.

However, removing the $\chi^{[k+1]}$ components (see Column 2 for Basis B), which mostly contribute to the dimension of the final polarized basis set, deteriorates the spectacular agreement between Column 3 for polarized Basis B and the results for Basis E. It should be also pointed out that the results calculated with polarized Basis A, which is derived from a minimal CGTO set, are at least qualitatively correct.

The effect of the basis set polarization can also be seen from the diminishing degree of violation of the sum rule (11). This sum rule is even better satisfied for completely polarized bases A and B than for Basis E.

In general, the quality of the dipole moment derivatives calculated with the aid of computationally convenient Eq. (9c) and the polarized basis B is at least competitive to the results obtained from the derivatives of the dipole moment function for Basis E. Also the results which follow from the polarized minimal basis set A are quite encouraging. It can also be seen from the data of Table 4 that the present technique provides a simultaneous improvement of the calculated dipole moments and intramolecular electric fields.

4. Summary and conclusions

The present proposal of polarized basis sets derived from relatively small highly contracted CGTO bases has been shown to result in the possibility of computing the dipole moment derivatives from the nuclear electric shielding factors. By the method of derivation of these basis sets the Hellmann–Feynman theorem with respect to $\underline{X}$ is only slightly violated and calculations based on Eqs. (9b) and (9c) become almost equivalent. The principal advantage of using Eq. (9c) follows from the fact that *all* dipole moment derivatives can be calculated by using *the same* set of molecular integrals. The same is obviously true for the use of Eq. (9c) with Basis E. However, the basis set comprises as much as 91 CGTO's while the corresponding numbers for completely polarized bases A and B are 26 and 52, respectively. This opens the possibility of accurate calculations of molecular dipole moment derivatives for much larger molecules.

In comparison with gradient techniques [4-6] the present method avoids the calculation of all derivatives of molecular integrals with respect to $X_{A\alpha}$ at the expense of the increased size of the basis set. Hence, according to the ratio timing/dimension, the polarized basis sets can be considered as either competitive or an alternative solution.

The concept of a polarized basis set derived from some standard initial set of CGTO's has previously been employed [11] in calculations of molecular dipole moments. A similar idea has also been exploited by Nakatsuji et al. [29] for the calculation of molecular force fields and force constants. All these approaches follow from the concept of perturbation-dependent basis sets. This dependence can be either exploited explicitly by using different forms of the gradient method [4–7, 16–18] or indirectly through the perturbation-oriented extension of standard bases. In both cases the quality of calculated properties appears to follow the quality of the energy calculated with the given initial basis set [30].

The concept of polarized basis set should above all be understood as a devise for the composition of suitable basis sets for accurate calculations of molecular properties. It is obvious that with high accuracy demands one has to use appropriately large basis sets. The method described in this paper will only help to define the form of the basis set extension for the given property. With lowered accuracy demands the present method can be efficiently employed in straightforward finite-field calculations according to Eq. (9c). As illustrated in the previous section even for the polarized minimal CGTO basis set the accuracy of the calculated data is quite satisfactory.

Finally, it should be mentioned that similar techniques, based on the interchange theorem and the concept of polarized basis sets can be used in calculations of other related properties, e.g. higher-order-derivatives of the dipole moment or derivatives of higher-order electric properties. In particular combining the present technique with that proposed for calculations of electric properties [11] can lead to highly accurate derivatives of the polarizability tensor and predictions of molecular Raman spectra.

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