MEDIUM-SIZE POLARIZED BASIS SETS FOR HIGH-LEVEL CORRELATED CALCULATIONS OF MOLECULAR ELECTRIC PROPERTIES

Andrzej J. SADLEJ

Theoretical Chemistry, Chemical Centre,
University of Lund, Box 124, S-221 00 Lund, Sweden

Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

The basis set polarization approach is applied to the generation of medium-size polarized GTO/CGTO basis sets for accurate calculations of molecular dipole moments and polarizabilities. The polarized basis sets determined in this paper for H and C through F are employed in SCF HF and MBPT calculations of dipole moments and polarizabilities of FH, H_2O, NH_3, and CH_4. The excellent results obtained at both the SCF HF and MBPT(4) levels of approximation indicate that the present basis sets can be employed for the accurate high-level correlated studies of relatively large molecules. The use of those basis sets in calculations of intermolecular interactions is also discussed.

This paper is dedicated to Dr Rudolf Zahradník in appreciation of his achievements in science and his leading role for quantum chemistry in Czechoslovakia.

Introduction

The majority of computational methods of quantum chemistry[1-3] employed nowadays in calculations of the electronic structure and properties of molecules are formulated in terms of many-electron wave functions which are built from some set of single-particle states (spin-orbitals)[4,5]. The determination of spin-orbitals is commonly carried out by expanding them into what is called a basis set, i.e., a set, in principle complete, of some known functions. The algebraic procedures involved in this step[6] require that in practice the basis sets used in molecular calculations are neither complete nor exhaustively large and flexible. For computational reasons relatively small basis sets are preferable. However, the basis set truncation is unavoidably followed by its reduced flexibility. Certain balance between the basis set size and its flexibility can be achieved in a number of different ways. Thus, a proper, purpose-oriented, choice of the basis set becomes one of the main issues in computational quantum chemistry and to a large extent affects the accuracy and reliability of the calculated data.

Most molecular calculations are currently performed with basis sets of nucleus-centred Gaussian-type orbitals (GTO's)[7,8]. They are known to offer several computational advantages[9] Moreover, the GTO basis sets are well standardized[10-14] and a vast amount of knowledge with regard to their performance in molecular calculations has been accumulated over the past years.

However, most of them have been determined in atomic SCF HF calculations. The optimized GTO exponents which follow from those calculations stress the importance of certain regions of the electron density distribution which are relevant for the atomic SCF HF energy. For heavily truncated GTO basis sets the description of the outer part of the electron density distribution is quite poor. This, however, can be to some extent remedied by adding a posteriori the so-called diffuse GTO's with relatively low orbital exponents[15].

Far more complicated and subtle appears to be the problem of what is known as the polarization functions[11-15]. Although they do not follow directly from the SCF HF calculations for atoms in the ground electronic state, their presence in atomic basis sets employed for molecules is known to be of utmost importance[13-15].

Given the type and number of polarization functions in the selected GTO basis set, their orbital exponents can be, in principle, optimized with respect to the total molecular energy. For quite obvious reasons such a procedure has a rather limited range of applicability. In most cases the orbital exponents of polarization functions are chosen according to the experience gained in calculations for small molecules[12-15]. Another source of their standardized values may follow from atomic calculations at the correlated level. In this respect the recent approach of Almlöf and Taylor[16] seems to be particularly appealing and successful.

With a limited number of polarization functions of the given type the energy-oriented optimization of their exponents will certainly favor those regions of the electron density distribution which are significant for the lowering of the total energy. Hence, the flexibility of polarized basis sets derived from the energy minimization criteria may not be sufficient for accurate calculations of molecular properties other than the total energy. This aspect of the basis set composition was first clearly recognized by Werner and Meyer[17].

The polarized GTO basis sets of Werner and Meyer[17] have been constructed by extending the standard atomic GTO basis sets[10] with several diffuse and polarization functions. The determination of orbital exponents has been formulated into a set of rules based on the previous computational experience and some optimization[17]. However, it has been found[17,18] that three different sets of d-type GTO's are needed for the first-row atoms in order to simultaneously achieve a high accuracy of the calculated molecular correlation energies, dipole moments and polarizabilities. This obviously brings about the dimensionality problem in calculations for molecules comprising a larger number of the first-row atoms. Hence, any reduction of the basis set size and, in particular, of the number of polarization functions, without a significant loss of the accuracy, is worth of consideration.

In this paper an alternative approach to a systematic determination of polarized GTO basis sets for the calculation of molecular electric properties will be presented. Our approach is based on what is called the basis set polarization method[19,20] which has been employed previously for the derivation of very large polarized GTO basis sets for highly accurate calculations of electric properties of small molecules[19-22]. The basis set polarization method, which is surveyed in the next section, assumes that the dependence of the basis set functions on the relevant external perturbation is known[20,23]. If so, the polarization functions for the given initial basis set can be determined without additional computations. Moreover, they can be compressed into a contracted form[20] with the contraction coefficients obtained directly from the atomic orbitals computed for the initial basis set.

In order to achieve a significant reduction of the final GTO basis set size a series of exploratory calculations of atomic polarizabilities have been carried out. The

results have led to a series of rules for the derivation of medium-size polarized GTO basis sets. The corresponding basis sets for H and C through F are given in the Appendix. The performance of those basis sets is exemplified in calculations of correlation energies, dipole moments and dipole polarizabilities for the first-row hydrides.

The Basis Set Polarization Method

The basis set polarization technique[20,23] for the determination of polarization functions in calculations of molecular properties follows from the consideration of a many-electron system in the presence of the appropriate external perturbation. The method is closely related to the Hellmann–Feynman theorem[24] and its violation for perturbation-dependent functions[25-27].

Let us assume that the unperturbed system is reasonably well described by using some finite set of basis functions $\{\chi_\mu\}$ which determine the spin-orbitals u_i of the form:

$$u_i = \sum_\mu c_{\mu i} \chi_\mu \,.$$ (1)

In the presence of the external perturbation the spin-orbitals become perturbation-dependent. In principle this dependence may occur through both the expansion coefficients $c_{\mu i}$ and the basis set functions. Hence, one can write the perturbed spin-orbitals in the following form[27]:

$$u_i(\lambda) = \sum_\mu c_{\mu i}(\lambda)\, \chi_\mu(\lambda)\,,$$ (2)

where λ is a convenient perturbation-strength parameter. Usually the perturbation dependence of u_i is shifted completely to the expansion coefficients and the basis set is assumed to be perturbation-independent, i.e., chosen and fixed in calculations for the unperturbed system. However, a well-known exception is given by the geometry dependence of the standard nucleus-centred basis sets[25,28]. An analytic form of the perturbation dependence of basis set functions can be also devised for perturbations due to external electric[29,30] and magnetic[31] fields.

Let us now recall that the first-order derivative of the total energy with respect to the perturbation parameter λ is given by:

$$\frac{\partial E(\lambda)}{\partial \lambda} = \langle \Psi^{(0)}|\mathbf{H}^{(0)}|\,\Psi^{(0)}\rangle + \left\langle \frac{\partial \Psi(\lambda)}{\partial \lambda}\,|\mathbf{H}^{(1)}|\,\Psi^{(0)}\right\rangle + \left\langle \Psi^{(0)}|\mathbf{H}^{(1)}|\,\frac{\partial \Psi(\lambda)}{\partial \lambda}\right\rangle,$$ (3)

where $\mathbf{H}^{(0)}$, $\mathbf{H}^{(1)}$, $\Psi^{(0)}$, and $\Psi(\lambda)$ are the unperturbed Hamiltonian, the relevant perturbation operator, the wave function of the unperturbed system, and the perturbed wave function, respectively. The derivatives are evaluated at $\lambda = 0$.

In order to simplify our analysis let us assume that both $\Psi^{(0)}$ and $\Psi(\lambda)$ are approximated in the form of a single Slater determinant. Then, as long as the basis set is perturbation-independent and the spin-orbitals used to build these determinants are obtained by solving the SCF HF equations, the last two terms of Eq. (3) will vanish and the Hellman–Feynman theorem will be satisfied[25-28]. In other words this occurs when both the unperturbed spin-orbitals, $u_i = u_i^{(0)}$, and the perturbed ones, $u_i(\lambda)$, are expanded into the same set of basis functions. If the given basis set is perturbation-dependent this condition can be approximately satisfied by augmenting the initial set $\{\chi_\mu^{(0)}\}$ of the unperturbed system by a set of the first-order derivatives of $\chi_\mu(\lambda)$ with respect to λ. Obviously, this procedure might be continued until the complete basis set limit is reached. However, with a reasonably large initial basis set $\{\chi_\mu^{(0)}\}$ the augmented basis set $\{\chi_\mu^{(0)}, \partial\chi_\mu(\lambda)/\partial\lambda\}$ is expected to make the last two terms of Eq. (3) negligibly small. The extension of the initial basis set can be carried out through higher orders in λ and results in what is called the polarized basis set. According to the present computational experience[19-23] the first-order extension appears to be quite sufficient for accurate calculations of the first- and second-order molecular properties.

A straightforward extension of the basis set would at least double its size and produce serious dimensionality problems for most but very small systems. However, a considerable reduction of the size of the final polarized basis set can be gained by considering the perturbed spin-orbitals (2). If the basis set is perturbation-dependent all dependence of $u_i(\lambda)$ on the perturbation strength can be in principle shifted to that of $\chi_\mu(\lambda)$. Then, the perturbed spin-orbitals can be approximately written as:

$$u_i(\lambda) \approx \sum_\mu c_{\mu i}^{(0)} \chi_\mu(\lambda) , \tag{4}$$

where $c_{\mu i}^{(0)} = c_{\mu i}(0)$ is the expansion coefficient determined in calculations for the unperturbed system. The approximate character of Eq. (4) follows from the fact that the perturbed spin-orbitals must satisfy the orthonormality conditions:

$$\langle u_i(\lambda) | u_j(\lambda) \rangle = \delta_{ij} \tag{5}$$

for any value of the perturbation strength. Since in general,

$$\langle \chi_\mu(\lambda) | \chi_\nu(\lambda) \rangle \neq \langle \chi_\mu^{(0)} | \chi_\nu^{(0)} \rangle , \tag{6}$$

the requirement (5) will affect to some extent the expansion coefficients in Eq. (4). However, through the first-order in λ this modification of $c_{\mu i}^{(0)}$ is not expected to be vitally important for the present method of the generation of polarized basis sets.

Within a single determinant approximation for the wave function the evaluation

of Eq. (3) with some perturbation-dependent basis set requires only the knowledge of the first-order perturbed occupied spin-orbitals[25−27] whose number, say n, is commonly much smaller than the dimension M of the initial basis set used for the unperturbed system. Hence, a suitable polarized basis set of the dimension $M + n$ can be generated as a union of $\{\chi_\mu^{(0)}\}$ and the set $\{u_i^{(1)}\}$ of the first-order derivatives of all occupied spin-orbitals:

$$u_i^{(1)} = \left(\frac{\partial u_i(\lambda)}{\partial \lambda}\right)_{\lambda=0} \approx \sum_\mu c_{\mu i}^{(0)} \left(\frac{\partial \chi_\mu(\lambda)}{\partial \lambda}\right)_{\lambda=0} , \quad i = 1, 2, \ldots, n \qquad (7)$$

which are obtained directly by the differentiation of Eq. (4). This procedure can be applied at the level of atomic SCF HF calculations and the additional basis functions $u_i^{(1)}$ can be considered as strongly contracted components of the polarized basis set. Depending on the size and flexibility of the initial basis set and the accuracy requirements the additional basis functions (7) can be to some extent decontracted, i.e., split into more than one function of the polarized basis set. Moreover, for the given form of the perturbation dependence of $\chi_\mu(\lambda)$ one usually finds[20,23] that the summation in Eq. (7) can be restricted to a rather limited number of terms. Also some of the new functions (7) may be expected to strongly overlap with those already present in the initial basis set, and thus, they can be safely removed from the final polarized set.

In this context one should recall that the aim of the present study is to derive relatively small basis sets for fairly accurate calculations of molecular properties. Hence, any possibility of a further reduction of the general polarized basis set defined in terms of Eq. (7) deserves a careful consideration. A very formal approach which follows from Eq. (7) would, in general, produce the polarized basis sets either excessively too sizable or insufficiently flexible.

The choice of a basis set for molecular calculations, independently of the accumulated knowledge, is always to some extent arbitrary and represents some kind of artistry. Most calculations are carried out by using purpose-oriented basis sets. Hence, there should be no harm in saying that the derivation of relatively small and useful polarized basis set must be accompanied by a series of exploratory studies. Some of those numerical experiments, which have been carried out at the level of atomic SCF HF calculations, are reported in the next section and concluded in the form of convenient rules.

Polarized Atomic GTO Basis Sets for Calculations of the Electric Dipole Properties

The main idea underlying the basis set polarization method discussed in the previous section follows from the assumption that the basis set functions may explicitly depend on the external perturbation. Once this dependence is known and the SCF HF eigen-

vectors of the unperturbed system are available, the polarization functions can be determined directly from Eq. (7). It is convenient to execute this procedure at the atomic level and then use the derived atomic basis sets in molecular calculations.

The basis set polarization method can be, in principle, used for any external perturbation, provided the analytic form of $\chi_\mu(\lambda)$ is given. The present study is limited to the consideration of the homogeneous electric field perturbation. The perturbation parameter λ will be identified with the components of the electric field strength $F = \{F_x, F_y, F_z\}$. It is also assumed that the initial basis set is built of GTO's.

The dependence of GTO's on the homogeneous electric field strength can be determined by analysing the corresponding results for the harmonic oscillator. It has been found[29] that the external electric field perturbation amounts approximately to a field-dependent shift of the orbital origin R:

$$R(F) = R(0) + \frac{1}{\alpha^2} F \frac{(\beta \cdot F)}{F}, \tag{8}$$

where F is the length of the electric field vector and α denotes the orbital exponent of the given GTO which is initially centred at $R(0)$. The vector $\beta = \{\beta_x, \beta_y, \beta_z\}$ is built of what is known as the scale factors[29]. Their meaning and the methods for their determination have been discussed elsewhere[27]. Since the scale factors enter the origin shift (8) in a product with the electric field strength, they are completely irrelevant for the derivation of $u_i^{(1)}$.

The differentiation of a field-dependent GTO, $\chi_\mu(\lambda) = \chi_\mu(F)$, with respect to some component F_σ ($\sigma = x, y, z$) of the electric field strength gives in general a combination of two new GTO's with the same orbital exponent[9]. For a normalized initial GTO χ^l which corresponds to the angular quantum number l and the orbital exponent α, the resulting combination of normalized GTO's will be

$$\left(\frac{\partial \chi^l(F)}{\partial F_\sigma}\right)_{F=0} = \alpha^{+1/2} \chi^{l-1}(0) + \alpha^{-1/2} \chi^{l+1}(0), \tag{9}$$

where the coefficients in front of the shifted downwards (χ^{l-1}) and upwards (χ^{l+1}) GTO's follow from the standard normalization of all basis functions[9,20].

It has been argued[20] that in the case of the external electric field perturbation the lowered component of the r.h.s. of Eq. (9) can be simply omitted. Its contribution will be large in the region close to the atomic nucleus and hence, relatively irrelevant in the present case. Within this approximation Eq. (7) becomes:

$$u_i^{(1)} \approx \sum_\mu c'_{\mu i} \chi_\mu^{l+1}, \tag{10}$$

where χ^{l+1} is the appropriate shifted upwards component of the derivative (9) and

$$c'_{\mu i} = c^{(0)}_{\mu i} \alpha_\mu^{-1/2} \; . \tag{11}$$

Thus, if Eq. (10) is recognized as a new contracted Gaussian-type orbital (CGTO), its contraction coefficients are completely determined by the eigenvectors of the unperturbed system and the orbital exponents of the initial GTO basis set. In what follows Eq. (10) will be considered as a pragmatic definition of polarization functions to be added to the $\{\chi^{(0)}_\mu\}$ basis set.

In our previous studies of the basis set polarization method[20,22] Eq. (11) was applied directly to either GTO's or CGTO's of the initial basis set. However, those studies were aimed at highly accurate calculations of electric properties[20,22] of diatomic molecules and the use of large polarized basis sets was quite obvious and necessary. In the present paper we aim at the determination of moderately large polarized GTO basis sets which might be employed in calculations of electric properties of much larger systems. With this purpose in mind some further reduction of the size of the $u_i^{(1)}$ set is quite desirable and may follow from the consideration of certain features of the initial GTO basis sets.

The present approach limits the polarization components to those which follow from the first-order derivatives of the initial perturbation-dependent basis set. At the level of the SCF HF approximation this should be sufficient for the calculation of electric properties through the third-order in the electric field strength[32] since in principle only the first-order perturbed wave function is needed for their evaluation[33]. In calculations at the correlated level one may need the polarization components through the same order as that of the calculated electric property[34,35]. However, it follows from several recent calculations[36,37] that at least for the calculation of electric dipole moments and dipole polarizabilities the higher-order polarization components of the given basis set are not highly important. The polarized basis sets generated in this study are meant to be used in calculations of molecular dipole moments and polarizabilities, and thus, the polarization components will be restricted to those which follow from the first-order derivatives of the initial basis set functions.

The preliminary steps of the generation of polarized atomic basis sets can be summarized as follows. First, we need to choose some reasonably good initial basis set which is known to provide sufficiently accurate description of the atomic ground state in the SCF HF approximation. In this paper our initial basis sets for H and C through F are the (5) and (9.5) atomic GTO basis sets of van Duijneveldt[11], respectively. In order to reduce the number of functions which are actually used in calculations they have been contracted to what is known as the double-zeta CGTO basis sets, i.e., $[5/2]$ for H and $[9.5/4.2]$ for C through F. The contraction schemes can be read from the tabular data presented in the Appendix.

Obviously, there is a great deal of arbitrariness in both the choice and contraction of the starting GTO basis set. The double-zeta GTO/CGTO basis sets are known to perform reasonably well in calculations of atomic and molecular energies[12-14] and appear to be a suitable choice for the present purposes. On the other hand, the energy-oriented optimization of orbital exponents makes those basis sets insufficiently diffuse. Hence, according to the above discussion, they need to be extended by some diffuse functions of the same type as those already present in the given basis set. This constitutes the second preliminary step in the generation of polarized basis sets. Its arbitrariness is quite obvious and depends also on the quality of the initial GTO/CGTO set.

In the present paper each shell $(s, p, ...)$ of the selected GTO/CGTO basis set is augmented by one diffuse GTO whose orbital exponent is determined by assuming that it forms an even-tempered sequence[17,38] with the exponents of the two most diffuse GTO's of the given shell of the original set. The additional diffuse GTO's are left uncontracted leading to the [6.3] and [10.6/5.3] GTO/CGTO basis sets for H and C through F, respectively. The SCF HF calculations have been performed with those basis sets in order to determine the expansion coefficients of Eq. (11).

On considering the polarization of the pre-processed GTO/CGTO basis set one should take into account that the polarization components which follow from the s-type SCF HF atomic orbitals are just the p-type CGTO's. Hence, for C through F, the polarization of $1s$ and $2s$ SCF HF orbitals will only result in augmenting the p-subset. Let us also note that according to Eq. (11) the weights of the p-type GTO's in the polarization function (10) derived from the s-type SCF HF orbitals are proportional to $\alpha_\mu^{-1/2}$. Therefore, not too much improvement of the description of the p shell will be gained, for anyway this shell is assumed to be reasonably well represented within the [10.6/5.3] GTO/CGTO basis sets. However, for the hydrogen atom the polarization function obtained from the $1s$ orbital will be of utmost importance.

The above considerations lead to the conclusion that for the calculation of electric properties only the outermost occupied atomic shell needs to be polarized. Thus, the application of the basis set polarization method to the hydrogen atom amounts to using Eq. (10) for the $1s$ orbital and results in a [6.6/3.1] polarized GTO/CGTO basis set. In a similar way we obtain the polarized [10.6.6/5.3.1] GTO/CGTO basis sets for C through F.

In order to study the performance of those polarized basis sets we have carried out a series of exploratory calculations of the dipole polarizability of the fluorine atom in the ^2P state by using the finite-field perturbation method. Those atomic calculations have been restricted to the SCF HF level of approximation with the purpose to investigate the efficiency and flexibility of the strongly contracted $(6 \rightarrow 1)$ d-type polarization function. We have also studied the possibility of removing some of the d-type GTO's from the polarization functions. The results of these investigations

are summarized in Table I. As regards the computational part of those calculations one should mention that the s-component of the cartesian d-type orbitals was removed from the basis set. The dipole polarizability values have been obtained from the SCF HF energies calculated with the electric field strength $F = 0.000$ a.u. and 0.002 a.u.* Our results are qualified against the most trusty SCF HF values of Voegel et al.[39] and Werner and Meyer[18].

The following conclusions can be drawn from the data of Table I. Above all the subset of six primitive d-type GTO's which follows from the polarization of the $2p$ SCF HF orbital appears to be unnecessarily too extensive. Removing even four d-type GTO's with the highest values of the orbital exponents has practically no influence on the calculated polarizabilities. However, if the polarized basis sets are to be used for calculations at the correlated level, some of the primitive d-type GTO's with higher orbital exponents might be needed[17]. For this reason a set of

TABLE I

Preliminary SCF HF studies of the basis set polarization scheme. Calculations of the dipole polarizability of $F(^2P)$. All results in a.u.

	Dipole polarizability	
Polarized basis set[a]	$M_L = 0$	$M_L = \pm 1$
$[10.6.6/5.3.1]^b$	2·997	3·156
$[10.6.4/5.3.1]^c$	2·997	3·156
$[10.6.2/5.3.1]^d$	2·997	3·157
$[10.6.4/5.3.2]^e$	3·044	3·319
$[10.6.4/5.3.3]^f$	3·094	3·385
Ref. 18	3·092	3·391
Ref. 39	3·117	3·355

[a] All contractions coefficients in the d subset follow from the $2p$ SCF HF orbital calculated with the $[10.6/5.3]$ GTO/CGTO basis set. See text for details. The specification of contractions given below assumes that the d-type GTO's are arranged in the order of decreasing orbital exponents.
[b] Complete contraction of the d-type function $(6 \rightarrow 1)$ according to Eq. (10). [c] Two d-type GTO's with the highest orbital exponents removed from the primitive basis set; the remaining four d-type GTO's contracted as $(4 \rightarrow 1)$. [d] Four d-type GTO's with the highest orbital exponents removed from the primitive basis set; the remaining two contracted as $(2 \rightarrow 1)$. [e] Two d-type GTO's with the highest orbital exponents removed from the primitive basis set; the remaining four d-type GTO's contracted as $(4 \rightarrow 2 + 2)$. [f] Two d-type GTO's with the highest orbital exponents removed from the primitive basis set; the remaining four d-type GTO's contracted as $(4 \rightarrow 2 + 1 + 1)$.

* 1 a.u. $= 5.1423 . 10^{11}$ V m^{-1}.

four d-type GTO's with the lowest values of orbital exponents has been retained in other exploratory calculations reported in Table I. However, the results obtained with the [10.6.4/5.3.1] basis set are not as satisfactory as they should be. In particular, a strong $(4 \rightarrow 1)$ contraction of the d-subset with the contraction coefficients derived from the $2p$ SCF HF orbital according to Eq. (10) does not reproduce well enough the polarizability anisotropy. The study of the effects of the decontraction show that in order to correctly obtain the polarizability anisotropy one needs to leave completely decontracted the two most diffuse d-type GTO's. This, however, results in a basis set which may already be too large for molecular applications.

On comparing the polarizability data calculated with the [10.6.4/5.3.2] and [10.6.4/5.3.3] GTO/CGTO basis sets one can conclude that the first of them does not assess correctly the weight of the most diffuse GTO in the corresponding contracted function. This is not surprising, since the contraction coefficients follow from the $2p$ SCF HF orbital calculated for the ground state of the fluorine atom. Those calculations tend to diminish the role of a diffuse p-type GTO added to the initial [9.5/4.2] basis set and this is reflected, through Eq. (10), in the form of the corresponding polarization function. Hence, in order to expose the role of the most diffuse d-type GTO one needs a $2p$ SCF HF orbital which stresses the importance of the outer region of the electron density distribution. The most natural way to accomplish this goal is to use the $2p$ SCF HF orbital of the ground state of the fluoride ion. Indeed, the results obtained with such a choice of the contraction coefficients in Eq. (10) and the contraction scheme $(4 \rightarrow 2 + 2)$ are completely acceptable $(\alpha(M_L = 0) = 3\cdot081$ a.u., $\alpha(M_L = \pm1) = 3\cdot374$ a.u.). Thus, the [10.6.4/ /5.3.2] GTO/CGTO basis set with partly decontracted polarization function (10) generated from the $2p$ SCF HF orbital of the fluoride ion apears to be a suitable candidate for the routine use in calculations of molecular electric properties.

An analogous series of calculations has been also performed for the ^3P state of the oxygen atom. The conclusions which follow from calculations of the electric dipole polarizability of $O(^3P)$ with differently truncated and contracted sets of polarization functions derived according to Eq. (10) are the same as those given for the fluorine atom. Hence, it appears to be possible to generalize them into a set of pragmatic rules for the determination of polarized basis sets. According to our study of the dipole polarizability of $F(^2P)$ and $O(^3P)$ the generation of a medium-size polarized basis set should proceed as follows:

(i) The given primitive GTO basis set[10-14] should be contracted to the minimal acceptable size. A double-zeta quality of the contracted set appears to be a reasonable choice.

(ii) The GTO/CGTO basis set should be extended by at least one diffuse function in each shell. The diffuse GTO's are left uncontracted and their exponents can be derived from the corresponding even-tempered sequences.

(iii) The polarization functions are to be generated only for the outermost occupied shell of the given atom. The contraction coefficients in Eq. (10) should be determined from the SCF HF eigenvectors of the nearest negative ion.

(iv) Several primitive GTO's with high orbital exponents can be removed from the polarization function. According to our experience it is advisable to retain at least two primitive polarization GTO's. If the calculations are to be carried out at the correlated level, retaining four primitive polarization GTO's with the lowest orbital exponents is recommended.

(v) A polarization function comprising four primitive GTO's should be decontracted into two CGTO's according to the contraction scheme $(4 \rightarrow 2 + 2)$. No decontraction is needed for polarization functions involving only two primitive GTO's.

Those rules and recommendations, when used for the first-row atoms with standard initial GTO basis sets of the form $(n_s . n_p)$, result either in the $[n_s + 1 . n_p + 1.2/5.3.1]$ GTO/CGTO basis sets which can be used in molecular calculations at the SCF HF level, or in the $[n_s + 1 . n_p + 1.4/5.3.2]$ GTO/CGTO basis sets for calculations at the correlated level. The latter ones, generated in this paper for $n_s = 9$ and $n_p = 5$, i.e., for the initial (9.5) GTO basis sets, are collected in the Appendix. All of them have been checked against the results for atomic dipole polarizabilities computed in the SCF HF approximation and the corresponding data are displayed in Table II.

The rules and recommendations derived in this paper seem to be equally well applicable for the generation of polarized basis sets for the second-row atoms. However, the hydrogen atom has been found to represent a rather specific case. In principle, all rules (i)−(v) can be applied for the generation of its polarized basis sets of the form $[n_s + 1.4/3.2]$ or $[n_s + 1.2/3.1]$, whose structure is compatible with that for the first-row atoms. If the size of the initial GTO basis set $(n_s = 5$ in the present study) is rather small, using the contraction coefficients determined from the $1s$ atomic orbital of H^- results in a very diffuse polarization function. This follows from the fact that in the SCF HF approximation the H^- ion is not stable with respect to $H + e^-$. Hence, in this particular case the polarization function has been determined directly from the GTO expansion of the $1s$ orbital of the hydrogen atom. The polarized basis set obtained in this way is given in the Appendix while the calculated polarizability value is shown in Table II. Most likely the same approach will have to be used for the determination of polarized basis sets for He, Ne, and perhaps also for Ar.

The data of Table II clearly indicate that the present method of the generation of polarized GTO/CGTO atomic basis sets gives the dipole polarizabilities which are very close to the numerical SCF HF data of Voegel et al.[39] and the near-HF values of Werner and Meyer[18]. It should be stressed that the present method does not involve any explicit, property-oriented, optimization of polarization func-

tions[17,40,42,43]. Once the initial GTO/CGTO basis set is chosen, the polarization functions follow directly from its dependence on the external electric field strength[29]. All parameters which enter the present definition of the polarized basis set either follow from the assumed GTO/CGTO set (orbital exponents and/or some of the contraction coefficients) or can be easily obtained from routine atomic SCF HF calculations (contraction coefficients).

In principle the present method can be applied to any selected GTO/CGTO basis set[20−23]. A similar procedure can also be used for other perturbations, provided the basis set dependence on the perturbation strength is known[23,30]. The additional rules derived in the present study have a purely pragmatic character. By supplementing the definition (10) of a general polarized basis set they help to reduce its size without a significant loss of the accuracy of the calculated electric properties.

The smaller polarized basis sets ([6.2/3.1] for H and [10.6.2/5.3.1] for C through F), which can be easily deduced from the data listed in the Appendix, appear to be suitable for less accurate calculations of molecular dipole moments and polarizabilities at the SCF HF level of approximation. The medium-size basis sets ([6.4/3.2]

TABLE II

Atomic SCF HF dipole polarizabilities. A comparison of the present polarized basis set calculations with the accurate reference data. All values in a.u.

Atom	Source	$\alpha(M_L = 0)$	$\alpha(M_L = \pm 1)$	α^a	$\Delta\alpha^b$
$H(^2S)$	This work^c	4·503		4·503	
	Exact^d	4·5		4·5	
$C(^3P)$	This work^e	9·98	12·80	11·86	2·81
	Ref. 18	10·10	13·05	12·07	2·95
	Ref. 39	10·10	13·00	12·03	2·90
$N(^4S)$	This work^e	7·332		7·332	
	Ref. 18	7·365		7·365	
	Ref. 39	7·436		7·436	
$O(^3P)$	This work^e	5·108	4·557	4·741	−0·551
	Ref. 18	5·142	4·587	4·772	−0·556
	Ref. 39	5·066	4·505	4·692	−0·561
$F(^2P)$	This work^c	3·081	3·374	3·276	0·293
	Ref. 18	3·092	3·391	3·291	0·299
	Ref. 39	3·117	3·355	3·276	0·238

^{a} Rotational average: $\alpha = \frac{1}{3}(\alpha(M_L = 0) + 2\alpha(M_L = \pm 1))$. ^{b} Anisotropy: $\Delta\alpha = \alpha(M_L = \pm 1) - \alpha(M_L = 0)$. ^{c} Calculated with the [6.4/3.2] polarized basis set of this paper. See Appendix. ^{d} Ref. 41. ^{e} Calculated with the [10.6.4/5.3.2] polarized basis set of this paper. See Appendix.

for H and $[10.6.4/5.3.2]$ for C through F), whose parameters are given in the Appendix, are recommended for accurate calculations of molecular electric properties by using high-level correlated methods[1-3,44]. Their efficiency in calculations of molecular dipole moments and polarizabilities will be documented in the next section.

Calculations of Molecular Dipole Moments and Polarizabilities with Polarized GTO/CGTO Basis Sets

in order to exemplify the performance of the medium-size polarized basis sets, which are listed in the Appendix, we have carried out a series of illustrative calculations for the standard set of the first-row hydrides, i.e., FH, H_2O, NH_3, and CH_4. The near-HF values for the dipole moments and polarizabilities of those molecules as well as the corresponding electron correlation corrections are well established[17,37,45-50]. The most complete set of the pertinent data follows from the calculations by Werner and Meyer[17].

The results reported in this paper have been obtained by using the SCF HF method and the many-body perturbation theory (MBPT) approach[2,4,34,44]. All molecular electric properties follow from the numerical differentiation of the appropriate field-dependent energies[34,45,51]. For all molecules and all directions of the external electric field the strength of external field employed in our calculations was equal to ± 0.002 a.u. The standard molecular geometries[51] are used throughout this paper.

The correlation corrections to dipole moments and polarizabilities have been computed through the fourth-order in the electron correlation perturbation by using the MBPT package of the Bratislava group[52,53] interfaced to the integral, SCF, 4-index transformation, and property packages of this laboratory. For the series of molecules studied in this paper the complete fourth-order MBPT treatment of the electron correlation effects is known to recover nearly all correlation contribution to the dipole moments and polarizabilities[37,47,48,50], provided large enough basis sets are used[36,37]. Hence, the fourth-order MBPT correlation corrections calculated with the polarized basis sets of this paper give directly a measure of the basis set quality and its appropriateness in high-level correlated calculations of molecular electric properties[54].

The calculated SCF HF energy values and the MBPT results for the valence-shell correlation energies are shown in Table III. Although the energy data are not of primary interest for this study, their comparison with the corresponding estimates of the HF-limit energies[55] and the estimated values of the valence-shell correlation energy[18,55] gives some idea about the performance of polarized basis sets in energy-oriented molecular studies. Obviously, the present results for both the SCF HF and valence-shell correlation energies must be inferior to those obtained with much larger basis sets[37,45-49,56] in energy-oriented calculations. However, our SCF HF

TABLE III

The total SCF HF and valence-shell correlation energies of FH, H_2O, NH_3, and CH_4. All values in a.u.

Molecule[a]	SCF HF energy			Valence-shell correlation energy				
	this work[b]	Ref. 17[c]	estimated HF limit[d]	this work[b,e]			Ref. 17[c,f]	est.[g]
				MBPT(2)	MBPT(3)	MBPT(4)		
FH	−100·0535	−100·0582	−100·072	−0·2102	−0·2115	−0·2202	−0·2271	−0·315
H_2O	−76·0529	−76·0553	−76·068	−0·2135	−0·2187	−0·2271	−0·2246	−0·306
NH_3	−56·2121	−56·2150	−56·226	−0·1960	−0·2087	−0·2161	−0·2149	−0·277
CH_4	−40·2034	−40·2082	−40·219	−0·1620	−0·1823	−0·1890	−0·1877	−0·238

[a] Molecular geometries used in this study are the same as those in Ref. 51 and may slightly differ from the ones employed in the reference calculations by other authors. [b] Calculated with the polarized GTO/CGTO basis sets given in the Appendix. [c] SCF HF results obtained with the GTO/CGTO basis B of Ref. 17. [d] Ref. 55. [e] The symbol MBPT(n) denotes the result calculated in the MBPT approach through the n-th order in the correlation perturbation. [f] Valence-shell correlation energies calculated in the CEPA-1 approach. [g] Estimates of the valence-shell correlation energy from Ref. 17 based on the data of Pople and Binkley[55].

energies seem to be reasonably close to the estimated near-HF values and the fourth-
-order MBPT treatment, MBPT(4), recovers about the same amount of the valence-
-shell correlation energy as that calculated by Werner and Meyer by using the
coupled electron pair approximation (CEPA)[17] and rather large GTO/CGTO basis
sets. The lower-order MBPT approximations, i.e., MBPT(2) and MBPT(3), give
also quite satisfactory results.

The dipole moment data for FH, H_2O, and NH_3 are presented in Table IV. The
results of this paper are compared with those of Werner and Meyer[17] and the
SCF HF and MBPT data calculated with much larger basis sets[37,45−47,50]. The
correlated dipole moment values which are used as a reference for the present results
are known to be very close to the experimental data, provided the vibrational cor-
rections are taken into account[17]. Hence, for the purpose of the present study
a comparison of our results with the accurate vibrationless data of other authors
appears to give a sufficient evaluation of the quality of the polarized GTO/CGTO
basis sets. A similar presentation of the dipole polarizability results is given in
Table V.

TABLE IV

Dipole moments of FH, H_2O, and NH_3. All values in a.u.

Molecule[a]	Method	This work[b]	Reference results	Ref. 17[c]
FH	SCF HF	0·7566	0·756076[d], 0·7568[e]	0·757
	Corr.[f]	−0·0590	−0·0591[g], −0·0479[h]	−0·054
H_2O	SCF HF	0·7810	0·7801[i], 0·784[j]	0·782
	Corr.[f]	−0·0620	−0·0631[i], −0·049[j]	−0·059
NH_3	SCF HF	0·6369	0·6370[k]	0·635
	Corr.[f]	−0·0467	−0·0472[k]	−0·040

[a] See footnote a to Table III. [b] Calculations with polarized basis sets given in the Appendix.
The correlation corrections to the dipole moment calculated in the fourth-order MBPT scheme.
The convergence pattern of the MBPT perturbation series is the same as that in other calcula-
tions with much larger basis sets[37,45−48,50]. [c] Calculations with the GTO/CGTO basis set B.
The correlation corrections correspond to the CEPA-1 approximation. [d] Numerical HF result[57].
[e] Calculations with a large GTO/CGTO basis set[47,50]. [f] Correlation correction to the dipole
moment. [g] The fourth-order MBPT result obtained in a large GTO/CGTO basis set[47,50].
[h] Approximate fourth-order MBPT result (SDQ-MBPT) without triple substitutions[45]. [i] Cal-
culations with a large GTO/CGTO basis set. The correlation correction to the dipole moment
computed in the fourth-order MBPT approximation[48,50]. [j] Large GTO/CGTO basis set cal-
culations. The correlation corrections calculated by using the SDQ-MBPT(4) method[46].
[k] SCF HF and MBPT(4) calculations with a large GTO/CGTO basis set[37].

The data collected in Tables IV and V clearly document the excellent performance of our polarized basis sets in calculations of molecular electric dipole moments and polarizabilities at both the SCF HF and MBPT(4) levels of approximation.

TABLE V

Dipole polarizabilities of FH, H_2O, NH_3, and CH_4. All values in a.u.

Molecule[a]		Method[b]	This work[c]	Reference results	Ref. 17[d]
FH	α_{xx}	SCF HF	4·45	4·48[e], 4·48[f]	4·47
		Corr.	0·92	0·85[e], 0·70[f]	0·81
	α_{zz}	SCF HF	5·73	5·74[e], 5·76[f]	5·76
		Corr.	0·78	0·76[e], 0·69[f]	0·80
H_2O	α_{xx}	SCF HF	9·19	9·17[g], 9·18[h]	9·04
		Corr.	0·98	0·92[g], 0·69[h]	0·77
	α_{yy}	SCF HF	7·83	7·91[g], 7·95[h]	7·99
		Corr.	1·76	1·66[g]. 1·35[h]	1·60
	α_{zz}	SCF HF	8·50	8·51[g], 8·47[h]	8·47
		Corr.	1·32	1·33[g], 0·99[h]	1·17
NH_3	α_{xx}	SCF HF	12·75	12·76[i], 12·73[j]	13·03[k]
		Corr.	1·01	0·97[i]	0·77
	α_{zz}	SCF HF	13·28	13·32[i], 13·24[j]	13·98[k]
		Corr.	2·38	2·34[i]	2·21
CH_4	α	SCF HF	16 01	16·10[l], 16·08[j]	16·00
		Corr.	0·58	0·49[m]	0·53

[a] See footnote *a* to Table III. The components of the polarizability tensor are defined as follows. HF: the molecule lies along the z axis, H_2O: the molecule lies in the xz plane with the symmetry axis along the z direction, NH_3: the C_3 symmetry axis coincides with the z direction. [b] The abbreviation "Corr." refers to the correlation correction to the given component of the dipole polarizability tensor. [c] Calculations with polarized basis sets given in the Appendix. The correlation corrections calculated by using the fourth-order MBPT method. The convergence pattern of the MBPT correlation perturbation series closely resembles that of other calculations with large GTO/CGTO basis sets[37,45−48,50]. [d] Calculations with the GTO/CGTO basis set *B*. The correlation corrections correspond to the CEPA-1 approximation. [e] Accurate SCF HF and MBPT(4) calculations with a large GTO/CGTO basis set[47,50]. [f] Calculations with a large GTO/CGTO basis set. The correlation contribution to the dipole polarizability tensor computed in the SDQ-MBPT(4) approximation[45]. [g] Accurate SCF HF and MBPT(4) calculations with a large GTO/CGTO basis set[48,50]. [h] Calculations with a large GTO/CGTO basis set. The correlation contribution to the dipole polarizability tensor computed in the SDQ-MBPT(4) approximation[46]. [i] Accurate SCF HF and MBPT(4) calculations with a large GTO/CGTO basis set[37]. [j] Ref. 58. [k] See comments in Refs 37 and 40. [l] SCF HF calculations in a large GTO/CGTO basis set[49]. [m] The correlation correction calculated by using the SD CI method and a rather small GTO/CGTO basis set[59].

Hence, the GTO/CGTO basis sets derived in this paper can be recommended for calculations of molecular electric properties for much larger systems with a guaranted high accuracy of the computed data.

To handle a basis set of several hundreds of CGTO's becomes nowadays almost routine. The polarized GTO/CGTO basis sets are strongly contracted and the size of the final CGTO sets is relatively small. The strong contractions will obviously affect the timing of the integral calculation. However, those are performed only once for the given molecule and the same set of one- and two-electron integrals is used in all perturbation calculations. Thus, it is the size of the CGTO basis set which plays a decisive role in determining the necessary computational resources.

In the present paper the calculation of the electron correlation contribution to molecular electric properties is considered at the level of the fourth-order MBPT approximation. Obviously, the polarized GTO/CGTO basis sets can be employed in calculations of molecular dipole moments and polarizabilities by using any trustworthy high-level correlated method[1-3,44,54]. It is quite certain that at the SCF HF level of approximation the results should be very close to the corresponding HF limits, while at the correlated level they should come close to the limits for the given model of the electron correlation effects[1-3,44,54].

Summary and Concluding Remarks

A general systematic method for the generation of polarization functions by using the basis set polarization approach has been presented and applied for the determination of medium-size polarized GTO/CGTO basis sets. The basis sets derived in this paper for H and C through F are listed in the Appendix. It is important to stress that all their parameters follow directly from the available GTO data and routine SCF HF calculations at the atomic level. No additional optimization of the basis set functions is necessary.

The present molecular calculations reveal that the medium-size polarized GTO/CGTO basis sets of this paper give a near-HF accuracy for the dipole moments and polarizabilities and perform exceptionally well at the correlated level. Hence, the basis sets derived in this study can be recommended for high-level correlated calculations of molecular electric properties. Because of a rather small dimension of those basis sets, the accurate calculations of dipole moments and polarizabilities become feasible for fairly large systems.

The calculation and prediction of molecular electric properties are closely related to the determination of intermolecular interaction energies[60]. As a matter of fact, this is one of the most important reasons for the corresponding investigations. Having this paper dedicated to Dr Rudolf Zahradník, the author is pleased to mention some preliminary results obtained for the hydrogen-bonded dimers at both the SCF HF and MBPT levels of approximation. The basis sets derived in this paper,

TABLE VI

Polarized GTO/CGTO basis sets for H and C through F

Atom	CGTO	GTO	s Subset[a] orbital exponent	contraction coefficient	p Subset[b] CGTO	GTO	orbital exponent	contraction coefficient	d Subset[c] CGTO	GTO	orbital exponent	contraction coefficient
H	1	1	33·865014	0·006068	1	1	1·1588	0·18844				
		2	5·094788	0·045316		2	0·3258	0·88242				
		3	1·158786	0·202846	2	1	0·1027	0·11780				
		4	0·325840	0·503709		2	0·0324	0·00420				
	2	1	0·102741	1·								
	3	1	0·0324	1·								
C	1	1	5 240·6353	0·000937	1	1	18·8418	0·013887	1	1	1·2067	0·26285
		2	782·20480	0·007228		2	4·15924	0·086279		2	0·3855	0·80430
		3	178·35083	0·036344		3	1·20671	0·288744	2	1	0·1219	0·65350
		4	50·815942	0·130600		4	0·38554	0·499411		2	0·0386	0·86360
		5	16·823562	0·318931								
	2	1	6·175776	0·438742	2	1	0·12194	1·				
		2	2·418049	0·214974	3	1	0·038568	1·				
	3	1	0·511900	1·								
	4	1	0·156590	1·								
	5	1	0·0479	1·								
N	1	1	8 104·0716	0·000802	1	1	26·868987	0·014478	1	1	1·7508	0·22477
		2	1 216·0215	0·006174		2	5·991227	0·091156		2	0·5605	0·65956
		3	277·23428	0·031233		3	1·750842	0·297420	2	1	0·1759	0·87136
		4	76·904023	0·115198		4	0·560511	0·493796		2	0·0552	0·70422
		5	25·874419	0·296951								
	2	1	9·346767	0·447349	2	1	0·175948	1·				
		2	3·579794	0·245003	3	1	0·055231	1·				
	3	1	0·739610	1·								
	4	1	0·222617	1·								
	5	1	0·067006	1·								

Atom	Grp	Prim	Exponent	Coeff	Grp	Prim	Exponent	Coeff	Grp	Prim	Exponent	Coeff
O	1	1	10 662·285	0·000799	1	1	34·856463	0·015648	1	1	2·3062	0·20270
		2	1 599·7097	0·006153		2	7·843131	0·098197		2	0·7232	0·57910
		3	364·72526	0·031157		3	2·306249	0·307768	2	1	0·2149	0·78545
		4	103·65179	0·115596		4	0·723164	0·492470		2	0·0639	0·53387
		5	33·905805	0·301552								
	2	1	12·287469	0·444870	2	1	0·214882	1·				
		2	4·756805	0·243172	3	1	0·063850	1·				
	3	1	1·004271	1·								
	4	1	0·300686	1·								
	5	1	0·090030	1·								
F	1	1	13 521·523	0·000801	1	1	44·147303	0·016509	1	1	2·9532	0·18354
		2	2 028·6916	0·006164		2	9·993426	0·103481		2	0·9186	0·51058
		3	462·37392	0·031244		3	2·953246	0·315418	2	1	0·2668	0·69925
		4	131·37366	0·116081		4	0·918597	0·489353		2	0·0775	0·42926
		5	42·974531	0·303589								
	2	1	15·571440	0·445904	2	1	0·266824	1·				
		2	6·032232	0·239115	3	1	0·077500	1·				
	3	1	1·307215	1·								
	4	1	0·388869	1·								
	5	1	0·115680	1·								

[a] Except for the most diffuse GTO all orbital exponents and contraction coefficients are taken from Ref. 11. The standard segmented contraction scheme is employed[15]. The orbital exponent of the most diffuse GTO is determined from the appropriate geometric progression. [b] Except for the most diffuse GTO all orbital exponents and contraction coefficients for C through F are taken from Ref. 11 and the standard segmented contraction scheme is employed[15]. The orbital exponent of the most diffuse p-type GTO for C through F is determined from the appropriate geometric progression. The p-type CGTO's of H are determined according to the method described in this paper. [c] All d-type polarization functions are obtained according to the method described in this paper.

as could have been expected, appear to be perfectly suited for the calculation of molecular interaction potentials. Because of their relatively small size they must obviously lead to a rather large basis set superposition error. However, the calculations of the electric properties of monomers show that the secondary basis set superposition effects[61] are completely negligible. In such a case the standard counterpoise correction[62] for the basis set superposition effect on the total energy becomes justified. Simply the basis set superposition does hardly affect the electric properties of monomrs and the dominant part of the basis set superposition effect goes into the improvement of the monomer energies. Indeed, the superposition-corrected interaction potential for the HF dimer calculated with the polarized basis sets of this paper agrees very well with the results of more accurate studies.

APPENDIX

The medium-size polarized basis sets for H and C through F derived in this paper are listed in Table VI. They have been employed in all molecular calculations reported above. Somewhat smaller and less efficient polarized basis sets can be derived from the data of Table VI by removing the polarization function which refers to the higher values of the GTO exponents.

REFERENCES

1. Diercksen G. H. F., Wilson S. (Eds): *Methods in Computational Molecular Physics*. Reidel, Dordrecht 1983.
   Dykstra C. E. (Ed): *Advanced Theories and Computional Approaches to the Electronic Structure of Molecules*. Reidel, Dordrecht 1983.
2. Čársky P., Urban M.: *Ab initio Calculations. Lecture Notes in Chemistry*, Vol. 16. Springer-Verlag, Berlin 1980.
3. Roos B. O.: Adv. Chem. Phys. *67*, 399 (1987).
4. Paldus J., Čížek J.: Adv. Quantum Chem. *9*, 105 (1975).
5. Paldus J. in: *Theoretical Chemistry. Advances and Perspectives* (H. Eyring and D. J. Henderson, Eds), Vol. 2, p. 131. Academic Press, New York 1976.
6. Roothaan C. C. J.: Rev. Mod. Phys. *23*, 69 (1951); *32*, 179 (1960).
7. Boys S. F.: Proc. R. Soc. London, A *200*, 542 (1950).
8. Huzinaga S.: J. Chem. Phys. *42*, 1293 (1965).
9. Saunders V. R. in: *Methods in Computational Molecular Physics* (G. H. F. Diercksen and S. Wilson, Eds), p. 1. Reidel, Dordrecht 1983.
10. Huzinaga S.: *Technical Reports*. Division of Theoretical Chemistry, University of Alberta, Edmonton, Canada 1970.
11. van Duijneveldt F.: IBM J. Res. Develop. *1971*, 945.
12. Huzinaga S., Andzelm J., Kłobukowski N., Radzio-Andzelm E., Sakai Y., Tatewaki H.: *Gaussian Basis Sets for Molecular Calculations*. Elsevier, New York 1984.
13. Hehre W. J., Radom L., Schleyer P. v R., Pople J. A.: *Ab initio Molecular Orbital Theory*. Wiley, New York 1986; and references therein.
14. Huzinaga S.: Comput. Phys. Rep. *2*, 279 (1985).

15. Dunning T. H., jr, Hay P. J. in: *Methods of Electronic Structure Theory* (H. F. Schaefer III, Ed.). Plenum Press, New York 1977.
16. Almlöf J., Taylor P. R.: J. Chem. Phys. *86*, 4070 (1987).
17. Werner H.-J., Meyer W.: Mol. Phys. *31*, 855 (1976).
18. Werner H.-J., Meyer W.: Phys. Rev., A *13*, 13 (1976).
19. Jaszuński M., Roos B. O.: Mol. Phys. *52*, 1209 (1984).
20. Roos B. O., Sadlej A. J.: Chem. Phys. *94*, 43 (1985).
21. Matos J. M. O., Malmqvist P.-A., Roos B. O.: J. Chem. Phys. *86*, 5032 (1987).
    Matos J. M. O., Roos B. O., Sadlej A. J., Diercksen G. H. F.: Chem. Phys. *119*, 71 (1988).
22. Diercksen G. H. F., Sadlej A. J.: Chem. Phys. Lett. *141*, 530 (1987).
23. Woliński K., Roos B. O., Sadlej A. J.: Theor. Chim. Acta *68*, 431 (1985).
24. Epstein S. T.: *The Variation Method in Quantum Chemistry*. Academic Press, New York 1974.
25. Gerratt J., Mills I. M.: J. Chem. Phys. *49*, 1719 (1968).
    Thomsen K., Swanstrøm P.: Mol. Phys. *26*, 735 (1973).
26. Sadlej A. J.: Mol. Phys. *34*, 731 (1977).
    Dodds J. L., McWeeny R., Sadlej A. J.: Mol. Phys. *34*, 1779 (1977).
27. Epstein S. T., Sadlej A. J.: Int. J. Quantum Chem. *15*, 147 (1977).
28. Pulay P. in: *Application of Electronic Structure Theory* (H. F. Schaefer III, Ed.), p. 153. Plenum Press, New York 1977.

    Helgaker T. U. in: *Geometrical Derivatives of Energy Surfaces and Molecular Properties* (P. Jørgensen and J. Simons, Eds), p. 1. Reidel, Dordrecht 1986.
29. Sadlej A. J.: Chem. Phys. Lett. *47*, 50 (1977); Acta Phys. Pol., A *53*, 297 (1978).
30. Woliński K., Sadlej A. J.: Chem. Phys Lett. *64*, 51 (1979).
31. Ditchfield R. in: *MTP International Review of Science. Physical Chemistry, Series One* (A. D. Buckingham, Ed.), Vol. 2, p. 91. Butterworth, London 1972; and references therein.
32. Buckingham A. D.: Adv. Chem. Phys. *12*, 107 (1967).
33. Stevens R. M., Pitzer R. M., Lipscomb W. N.: J. Chem. Phys. *38*, 550 (1963).
    Diercksen G., McWeeny R.: J. Chem. Phys. *44*, 3554 (1966).
34. Sadlej A. J.: J. Chem. Phys. *75*, 320 (1981).
35. Sadlej A. J.: Int. J. Quantum Chem. *23*, 147 (1983); Acta Phys. Pol., A *59*, 669 (1981).
36. Diercksen G. H. F., Sadlej A. J.: Chem. Phys. *96*, 17, 43 (1985).
37. Diercksen G. H. F., Sadlej A. J.: Mol. Phys. *57*, 509 (1986).
38. Wilson S. in: *Methods in Computational Molecular Physics* (G. H. F. Diercksen and S. Wilson, Eds), p. 95. Reidel, Dordrecht 1983.
39. Voegel T., Hinze J., Tobin F.: J. Chem. Phys. *70*, 1107 (1979).
40. van Duijneveldt-van de Rijdt J. G. C. M., van Duijneveldt F. B.: J. Mol. Struct. (THEOCHEM) *89*, 185 (1982).
41. Allen L. C.: Phys. Rev. *118*, 167 (1960).
42. Diercksen G. H. F., Sadlej A. J.: Theor. Chim. Acta *63*, 69 (1983).
43. Kołos W.: Theor. Chim. Acta *51*, 219 (1979).
44. Bartlett R. J.: Annu. Rev. Phys. Chem. *32*, 359 (1981).
    Kucharski S. A., Bartlett R. J.: Adv. Quantum Chem. *19*, 262 (1985).
45. Bartlett R. J., Purvis III G.D.: Phys. Rev., A *20*, 1313 (1979).
46. Purvis G. D., Bartlett R. J.: Phys. Rev., A *23*, 1594 (1981).
47. Diercksen G. H. F., Kellö V., Sadlej A. J.: Chem. Phys. Lett. *95*, 226 (1983).
48. Diercksen G. H. F., Kellö V., Sadlej A. J.: J. Chem. Phys. *79*, 2918 (1983).
49. Diercksen G. H. F., Sadlej A. J.: Chem. Phys. Lett. *114*, 187 (1985).
50. Diercksen G. H. F., Roos B. O., Sadlej A. J.: Int. J. Quantum Chem., Quantum Chem. Symp. *17*, 265 (1983).

51. Diercksen G. H. F., Sadlej A. J.: J. Chem. Phys. *75*, 1253 (1981).
52. Urban M., Hubač I., Kellö V., Noga J.: J. Chem. Phys. *72*, 3378 (1980).
53. Noga J.: Comput. Phys. Commun. *29*, 117 (1983).
54. Salter E. A., Sekino H., Bartlett R. J.: J. Chem. Phys. *87*, 502 (1987).
55. Pople J. A., Binkley J. S.: Mol. Phys. *29*, 599 (1975).
56. Pople J. A., Frish M. J., Luke B. T., Binkley J. S.: Int. J. Quantum Chem., Quantum Chem. Symp. *17*, 307 (1983).
57. Laaksonen L., Pyykkö P., Sundholm D.: Comput. Phys. Rep. *4*, 313 (1986).
58. Lazzeretti P., Zanasi R.: J. Chem. Phys. *74*, 5216 (1981).
59. Amos R.: Mol. Phys. *38*, 33 (1979).
60. Hobza P., Zahradník R.: *Weak Interactions in Chemistry and Biology.* Elsevier, New York 1980.
61. Karlstrøm G., Sadlej A. J.: Theor. Chim. Acta *61*, 1 (1982).
62. Boys S. F., Bernardi F.: Mol. Phys. *19*, 553 (1970).