STANDARDIZED MEDIUM-SIZE BASIS SETS FOR CALCULATIONS OF MOLECULAR ELECTRIC PROPERTIES: GROUP IIIA

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The authors dedicate this paper to their friends, companions, and collaborators, Professor Petr Čársky of Prague and Professors Ivan Hubač and Miroslav Urban of Bratislava, on the occasion of all of them turning sixty in the year 2002. It is our pleasure to honor their outstanding achievements in science and in particular their contribution to the survival and development of quantum chemistry after the Soviet invasion of Czechoslovakia in 1968.

The idea of what is called the basis set polarization method is reviewed and the available polarized basis sets are surveyed. Following the basis set polarization approach and certain empirical rules developed earlier, the first-order polarized basis sets for the Group IIIA elements are generated. These basis sets have been developed for both nonrelativistic and spin-averaged Douglas–Kroll relativistic calculations. Their performance is tested in calculations of atomic dipole polarizabilities and in high-level-correlated calculations of the dipole moments of GaF, InF, and TlF. The relativistic effects have been found to significantly affect the calculated molecular dipole moments of the studied fluorides. The results are in satisfactory agreement with reference data. The present study completes the library of the first-order polarized basis sets for all atoms of the main groups of the Periodic Table.
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At present, most of computational quantum chemistry is formulated in terms of the algebraic approximation with all operators substituted by their matrix representations in some finite-dimensional set of what is called the basis functions[1–3]. The choice of either one-electron or many-electron basis set functions, *i.e.,* the choice of the computationally affordable and simultaneously accurate matrix representation of operators pertinent to the given problem is one of the main issues of computational quantum chemis-

try[2]. This choice is usually made at the level of the one-electron approximation and to a large extent determines the outcome of calculations.

The accuracy of the finite-dimensional algebraic approximation is strongly affected by the analytic features (shape) of functions used to build the one-electron basis set. Nowadays computational quantum chemistry is almost exclusively based on the use of Gaussian functions[4] whose analytic features are far from being the most suitable ones for the representation of atomic and molecular wave functions[5]. This is compensated by two factors. First, Gaussians are known to form a complete set[5] and one may expect that large enough Gaussian basis sets should be able to cope with the so-called cusp problem at the nucleus and simultaneously would give accurate enough form of the wave function in regions far away from the nuclei. Second and presumably more important is the easiness of the calculation of matrix elements of one- and two-electron operators[4,6].

The completeness of Gaussians is, however, not very helpful in applications since the Gaussian expansions exhibit relatively slow convergence[5]. In spite of the easiness with which the integrals required in molecular calculations can be computed, the length of the Gaussian expansion, *i.e.* the size of the Gaussian basis set required for the assumed level of accuracy, shortly becomes forbidding. A compromise is reached by the optimization of parameters (orbital exponents) which define the primitive basis set functions.

The optimization of the selected finite-dimensional basis set is usually based on the variational minimum energy criterion[7–9] and leads to energy-optimized basis sets. This can be accomplished either at the level of the Hartree–Fock (HF)[1–3] or post-HF [10,11] methods. The past decade has witnessed important developments[11–16] in this area with the roots in earlier papers by Jankowski *et al.*[17,18], Ruedenberg *et al.*[19–21], and Almlöf and Taylor[10].

In this context, particularly useful are the systematic procedures for the generation of Gaussian basis sets of increasing size and flexibility devised by Dunning[11]. Moreover, the systematically extended correlation-consistent basis sets of Dunning *et al.*[11–16] offer the possibility of the extrapolation of the calculated energies to the complete basis set (CBS) limit. The obvious price one pays is the very large basis set size which makes the correlation-consistent basis sets of limited use in routine molecular applications. There are also some additional aspects of this problem which make it worthwhile to develop smaller basis sets for specific calculations of acceptable accuracy.

The energy-oriented optimization of the given finite dimensional set of (Gaussian) basis functions stresses the importance of the matrix representa-

tion of those operators which enter the mean energy expression. The basis sets determined in such a way may not be the best ones to use for representing the operators which are related to other than energy properties of the system. Obviously, with large and flexible enough set of functions, all operators of interest may be given sufficiently accurate matrix representation. However, this soon makes the dimensionality of the algebraic problem and/or the timing of calculations going beyond the commonly available resources and acceptable times of execution. Particularly difficult is the calculation of molecular electric properties[15] and their notoriously slow convergence to the CBS limit is well illustrated by the recent data of Kobus *et al.*[22] On the other hand, atomic and molecular electric properties are the most useful data with a variety of applications[23,24] and methods for their routine and reliable calculation are certainly needed.

Although we fully recognize and appreciate the importance of all methods which give or may give the most accurate, benchmarking data for atomic and molecular properties[15,22], the approach followed in this paper is based on the philosophy which anticipates certain sacrifices. What is sacrificed is the goal of achieving the highest accuracy of the calculated data; the estimated accuracy of a few per cent for molecular (low-order) multipole moments and polarizabilities is considered to be satisfactory. Some gains are expected, however, and among them one should list the computationally acceptable dimensionality of the algebraic problem and the possibility of handling large, chemically interesting, molecules. This was the main idea underlying the development of specifically tailored basis sets for the use in high-level-correlated calculations of molecular dipole moments and dipole polarizabilities[25]. By the method of their generation[26–28], these electric-property-oriented basis sets are referred to as the *polarized basis sets* (PolX, where X stands for the symbol of the element).

It is particularly pleasing that the first paper on the generation of PolX basis sets was also published in this journal[25] and on the occasion at least as remarkable as the present one[29]. Since then the PolX basis sets have been generated for most of the main group atoms[30–36] as well as for elements of Groups IB and IIB[37,38] and rare gas atoms[39]. Due to their relatively small size and remarkable efficiency in calculations of molecular dipole moments, dipole polarizabilities, and related electric properties[40], the PolX sets have gained over the years certain recognition among computational chemists.

A new generation of PolX basis sets which offers a more compact treatment of contractions has been more recently reported by Pluta and one of the present authors[39] and is available through anonymous ftp[41] and on the web[42]. In calculations of molecular energies, dipole moments, and dipole

polarizabilities, the new PolX sets give essentially the same results as the earlier ones. However, their structure is better adapted to the requirements of the integral code Seward of the MOLCAS system of quantum chemistry programs[43]. One should add that extensions[39] of PolX bases to the so-called HyPolX sets for calculations of molecular hyperpolarizabilities are also available[41,42,44].

The early PolX basis sets have been developed under the assumption of the nonrelativistic hamiltonian. For heavy elements the relativistic effects could have been accounted for perturbationally[35–38] by using the Pauli approximation[45,46]. With the increasing interest in relativistic methods going beyond the Pauli approximation, the polarized basis sets have been developed[47,48] also for calculations within the Douglas–Kroll (DK) method[49–52]. These basis sets are labeled as PolX_dk and differ from their nonrelativistic counterparts by contraction coefficients. The "relativistic" PolX_dk basis sets are available for all first- and second-row atoms, for atoms of Groups IB and IIB [47], for alkali and alkaline-earth metal atoms[48] and can be accessed either by anonymous ftp [53] or on the web [54]. Several other unpublished[44,55] PolX_dk basis sets are available there as well[56].

Upon scanning the list of the available PolX and PolX_dk basis sets and their HyPolX counterparts, one can easily note that for the Group IIIA atoms, these basis sets are so far (and only recently) determined solely for boron and aluminium[39]. The absence of the corresponding basis set data for Ga, In, and Tl as well as the long-lasting absence of PolX bases for B and Al reflects certain problems which occur in their generation. These problems follow from particular features of the electronic structure of the Group IIIA elements; the generation of polarization functions needs to take into account also the next-to-valence shell whose contribution to atomic polarizabilities is not that small as in the case of the Group IVA through Group VIIIA elements. This to some extent resembles the problems encountered in the generation of PolX [31,34,36] and PolX_dk [48] basis sets for alkali and alkaline-earth metal atoms.

In the case of the Group IIIA elements, one needs to generate polarization functions for the valence s and p shells and the p (or d) subvalence shell while simultaneously keeping the total basis set size acceptably small. This is to be accompanied by the requirement that basis sets for the Group IIIA elements should have similar structure and flexibility as the PolX sets in the same row of the Periodic Table. Otherwise some artificial "overpolarization" of bonds may occur. These problems appear to have found satisfactory solutions in the present study and the resulting PolX and

PolX_dk sets become now available for all elements of the main groups of the Periodic Table.

We will review the method used to generate polarized basis sets with particular attention given to the above-mentioned problems which occur for the Group IIIA elements. The derivation of the PolX basis sets for non-relativistic calculations and PolX_dk sets (X = B, Al, Ga, In, Tl) for the use in DK relativistic studies will be presented and followed by testing their accuracy in calculations of atomic dipole polarizabilities. High-level-correlated nonrelativistic and relativistic studies of molecular dipole moments and some other electric properties of the Group IIIA fluorides will also be presented.

THE DEVELOPMENT OF POLARIZED BASIS SETS. SURVEY OF THE METHOD

The principles of the method used to generate polarized basis sets are rooted in the concept of the dependence of basis functions on the perturbation applied to the system. Particular cases of this idea, although not phrased explicitly, are as old as quantum chemistry. The earliest example goes back to Heitler and London[57], whose calculations of the potential energy curve of H_2 profited from the use of the nucleus-centered basis functions; the set of two hydrogenic 1s orbitals was allowed to "float" with the change of the internuclear distance expressing in that way the basis set dependence on molecular geometry. Later on, this idea was generalized by Gerratt and Mills[58], Thomsen and Swanstrøm[59], and developed by Pulay[60] into powerful tools of what is known as the gradient techniques for the optimization of molecular geometries[61–63].

In the case of perturbations by magnetic field, the explicit basis set dependence on the magnetic field strength was introduced by London[64] in the form of phase factors and contributed to the development of what is known as the gauge invariant atomic basis sets (GIAO)[65] and perturbation techniques based on their use[66].

The early attempts to introduce explicitly the electric-field dependence into one-electron basis functions were limited to their multiplicative forms[67–69]. A simple exponential form of the electric-field dependence of atomic orbitals was proposed by Moccia[70] and then extended by Hudis and Ditchfield[71]. In both cases the field-dependent exponential factor[70,71] makes the resulting electric-field-dependent orbitals not L^2-integrable. Thus, they can be used only in explicitly expanded form.

The electric-field dependence of the basis set functions based on the solution of the harmonic oscillator in external electric field was introduced by

one of the present authors[26,27] and later on has led to the development of polarized basis sets[25,30]. The main idea was to exploit the known electric-field dependence of solutions of the harmonic oscillator in external electric field **F** and the close relation between these solutions and commonly used Gaussian basis sets. In the case of a cartesian Gaussian function whose origin in the absence of an external electric field (**F** = 0) is at **A(0)**,

$$\chi(\mathbf{r}, \mathbf{A(0)}) = f(\mathbf{r} - \mathbf{A(0)}) \exp\left[-\alpha(\mathbf{r} - \mathbf{A(0)})^2\right] , \tag{1}$$

where α is the orbital exponent, the dependence on the homogeneous static external electric field can be expressed in terms of the field-dependent origin shift, *i.e.,*

$$\mathbf{A(0)} \rightarrow \mathbf{A(F)} = \mathbf{A(0)} - \frac{1}{\alpha^2} \beta \mathbf{F} , \tag{2}$$

where β is a scale factor whose value for the isotropic harmonic oscillator is equal to 0.25.

In the case of atomic or molecular calculations with electric-field-dependent Gaussian basis sets,

$$\{\chi_\mu(\mathbf{r}, \mathbf{A(F)}, \beta)\} , \tag{3}$$

the value of β can be optimized with respect to the second-order perturbed energy[26,27,72–74]. This was the method used in early applications of electric-field-variant (EFV) basis sets (*3*). For initial (field-independent) Gaussian basis sets of double-zeta or similar quality, the optimized values of β were found to be close to 0.1 and they did not significantly depend on the studied system.

The need for analytic determination of integral derivatives[75] and the optimization of the scale factor have turned our attention to other ways of benefiting from the analytic electric-field-dependence of Gaussian basis sets (*3*) which would permit the use of routine methods of perturbation theory.

The field dependence of the basis (*3*) shows how the given initial set (*1*) should be modified in the presence of the external electric field perturbation. This effect can be analysed in terms of the Taylor expansion of each field-dependent basis function. Let the primitive nucleus-centered Gaussian

function $\chi_\mu^{(l)}(\mathbf{r}, \mathbf{A(F)}, \beta)$ correspond to some value l of the angular momentum function. Then, its Taylor series expansion with respect to the F_σ component of the electric field strength $\mathbf{F}$ has the following form:

$$\chi_\mu^{(l)}(\mathbf{r}, \mathbf{A(F)}, \beta) = \chi_\mu^{(l)}(\mathbf{r}, \mathbf{A(0)}) + \sum_{p=1}^{\infty} \frac{1}{p!} (\beta F_\sigma)^p \chi_\mu^{(l,p)}(\mathbf{r}, \mathbf{A(0)}) , \qquad (4)$$

where the derivative functions $\chi_\mu^{(l,p)}(\mathbf{r}, \mathbf{A(0)})$,

$$\chi_\mu^{(l,p)}(\mathbf{r}, \mathbf{A(0)}) = \frac{1}{\beta^p} \left(\frac{\partial^p \chi_\mu^{(l)}(\mathbf{r}, \mathbf{A(F)}, \beta)}{\partial F_\sigma^p} \right)_{\mathbf{F}=0} \qquad (5)$$

are independent of the parameter β.

Let us note that through some n-th order with respect to F_σ, the addition of functions

$$\chi_\mu^{(l,1)}(\mathbf{r}, \mathbf{A(0)}), \ \ \chi_\mu^{(l,2)}(\mathbf{r}, \mathbf{A(0)}), ..., \chi_\mu^{(l,n)}(\mathbf{r}, \mathbf{A(0)}) \qquad (6)$$

to the initial field-independent basis set will be essentially equivalent to the use of explicitly field-dependent functions (*3*). Thus, the derivative functions (*5*) can be recognized as the *polarization functions* of the order p.

The unlimited process of adding derivative functions (*5*) through some selected value of $p = n$ would obviously give "polarized" basis sets of prohibitively large size. Some limitation of the basis size increase can be achieved by referring to general features of the initial field-independent basis sets commonly used in molecular calculations[76].

First, let us note that for the given value of l the p-th order polarization function corresponding to $\chi_\mu^{(l)}(\mathbf{r}, \mathbf{A(0)})$ will comprise Gaussian functions with the angular momentum quantum numbers in the range $|l - p|$, $|l - p + 2|$ through $l + p$. If the generation of polarization functions is carried out systematically for $p = 1, 2, ..., n$ then in the first step one obtains[6]

$$\chi_\mu^{(l,1)}(\mathbf{r}, \mathbf{A(0)}) \ \frac{1}{\beta} \left(\frac{\partial \chi_\mu^l(\mathbf{r}, \mathbf{A(F)}, \beta)}{\partial F_\sigma} \right)_{\mathbf{F}=0} =$$

$$= \alpha_\mu^{-1/2} \chi_\mu^{l-1}(\mathbf{r}, \mathbf{A(0)}) \delta_{l,0} + \alpha_\mu^{-1/2} \chi_\mu^{l+1}(\mathbf{r}, \mathbf{A(0)}) , \qquad (7)$$

where χ_μ^{l-1} and χ_μ^{l+1} denote *normalized* field-independent primitive Gaussians of the angular momentum $l - 1$ and $l + 1$, respectively.

With the usual structure of Gaussian basis sets one may expect that suitable GTOs for the angular quantum number equal to $l - 1$ already exist in the initial set. Thus, it should be sufficient to supplement the initial set only with the χ_μ^{l+1} component of $\chi_\mu^{(l,1)}$. Similarly, for higher-order derivative functions $\chi_\mu^{(l,p)}$, $p = 2, 3, ..., n$, the additional polarization functions will correspond to the highest value of the angular momentum quantum number, *i.e. $l + p$.* The primitive Gaussians for $|l - p|$, $|l - p + 2|$, ..., $|l + p - 2|$ are either covered by the initial set or were generated for lower values of p. This will certainly limit the size of the resulting p-th order polarized set of uncontracted Gaussian functions. Additional reduction can be achieved by applying the basis set "polarization" process at the level of atomic orbitals (eigenvectors) determined in Gaussian basis sets[28].

One should recognize that the method of the generation of polarization functions from the assumed electric-field dependence of the primitive Gaussian basis can be directly applied to *any* linear combination of Gaussian functions and in particular to atomic eigenvectors. The latter can be recognized as a particular case of the so-called *contracted* Gaussian orbitals (CGTOs). With the restriction that only the polarization functions with increased value of the angular momentum quantum number are saved, such method will produce a set of compact polarization functions. This method can be applied to any set of atomic eigenvectors, *e.g.* occupied atomic SCF HF, MC SCF, or approximate natural orbitals[77,78]. For the sake of clarity we shall limit our considerations to the set of atomic SCF HF eigenvectors which are sufficient to build the ground-state Slater determinant(s) for the given atom.

With the field-dependent basis set (*3*), the atomic one-electron eigenvector $u_k^l(\mathbf{r}, \mathbf{A(F)}, \beta)$ for the angular momentum quantum number l, can be written in the form

$$u_k^l(\mathbf{r}, \mathbf{A(F)}, \beta) = \sum_\mu c_{\mu k}\chi_\mu^l(\mathbf{r}, \mathbf{A(F)}, \beta) \,. \tag{8}$$

In general the expansion coefficients $c_{\mu k}$ will depend on the external field. However, under the assumption that most of the electric-field dependence is accounted for by the basis set functions (*3*), one can consider these coefficients as approximately independent of the external electric field

strength[79]. Then, upon expanding (*8*) into the Taylor series with respect to the σ component of the electric field strength, F_σ:

$$u_k^l(\mathbf{r}, \mathbf{A(F)}, \beta) = u_k^l(\mathbf{r}, \mathbf{A(0)}) + F_\sigma \left(\frac{\partial u_k^l(\mathbf{r}, \mathbf{A(F)}, \beta)}{\partial F_\sigma} \right)_{F=0} +$$

$$+ \frac{1}{2} F_\sigma^2 \left(\frac{\partial^2 u_k^l(\mathbf{r}, \mathbf{A(F)}, \beta)}{\partial F_\sigma^2} \right)_{F=0} + ..., \tag{9}$$

one recognizes that for each value of $p = 1, 2, ...$ the derivative terms

$$\frac{1}{\beta^p} \left(\frac{\partial^p u_k^l(\mathbf{r}, \mathbf{A(F)}, \beta)}{\partial F_\sigma^p} \right)_{F=0} = u_k^{(l, p)}(\mathbf{r}, \mathbf{A(0)}) \tag{10}$$

can be considered as new (contracted) functions which need to be added to the initial basis set of atomic orbitals.

The β-independent functions $u_k^{(l, p)}$ defined by Eq. (*10*) arise from the field-induced polarization effect on the initial basis set of atomic one-electron eigenvectors and can be referred to as the general *p*-th-order contracted polarization functions. Within this approach the β parameter does not affect the shape of polarization functions and does not need to be specified. If the extension of the initial set of eigenvectors (*8*) were carried out systematically, the resulting extended set would in general comprise the original field-independent CGTOs and all their derivatives (*10*) through certain order *n* with respect to the external electric field.

Under the assumption of field-independent contraction coefficients, the polarization CGTOs can be expressed in terms of the appropriate derivatives of primitive functions (*3*):

$$u_k^{(l, p)}(\mathbf{r}, \mathbf{A(0)}) \approx \frac{1}{\beta^p} \sum_\mu c_{\mu k} \left(\frac{\partial^p u_k^l(\mathbf{r}, \mathbf{A(F)}, \beta)}{\partial F_\sigma^p} \right)_{F=0}. \tag{11}$$

If the primitive Gaussian functions in (*11*) correspond to some value *l* of the angular momentum quantum number, then their *p*-th-order derivative will be expressed in terms of primitive Gaussians with the angular momentum quantum number ranging from $|l - p|$ through $l + p$. However, it has been already pointed out that primitive Gaussians with angular momentum quantum number lower than $l + p$ are either present in the original basis set or were generated in earlier steps of the systematic generation of the

lower-order polarization functions. Hence, the derivative in Eq. (*11*) can be approximately substituted by a normalized Gaussian function $\chi_\mu^{l+p}(\mathbf{r}, \mathbf{A(0)})$ which corresponds to the angular momentum quantum number $l + p$:

$$\frac{1}{\beta^p}\left(\frac{\partial^p \chi_\mu^l(\mathbf{r}, \mathbf{A(F)}, \beta)}{\partial F_\sigma^p}\right)_{\mathbf{F}=0} \approx \alpha_\mu^{-p/2} \chi_\mu^{l+p}(\mathbf{r}, \mathbf{A(0)}) . \tag{12}$$

Within this approximation the *p*-th-order polarization CGTO of Eq. (*11*) assumes the following form:

$$u_k^{(l,p)}(\mathbf{r}, \mathbf{A(0)}) \approx \sum_\mu c_{\mu k}\alpha_\mu^{-p/2}\chi_\mu^{l+p}(\mathbf{r}, \mathbf{A(0)}) = v_k^{(l,p)}(\mathbf{r}, \mathbf{A(0)}) , \tag{13}$$

where the factors $\alpha_\mu^{-p/2}$ appear owing to the renormalization of derivatives of the primitive Gaussian functions.

According to the method described so far, the *p*-th-order polarized set generated from occupied HF SCF orbitals u_k^l, $k = 1, 2, ..., n$ would comprise $(p + 1) \times n$ CGTOs, *i.e.*,

$$u_k^{(l)}(\mathbf{r}, \mathbf{A(0)}),\ v_k^{(l,1)}(\mathbf{r}, \mathbf{A(0)}), ..., v_k^{(l,p)}(\mathbf{r}, \mathbf{A(0)}) . \tag{14}$$

To further reduce the dimensionality of this *p*-th-order polarized basis set we will introduce additional approximations whose meaning and validity are supported either by the character of the perturbation operator or by the structure of commonly employed Gaussian basis sets.

First, one needs to recognize that the overwhelming contribution to polarization effects comes from the valence atomic shells. In some particular cases also the polarization contribution due to next-to-valence shell may be of importance. Hence, in general one needs polarization functions only for a few outer orbitals.

Second, let us note that for the valence shell with certain value *l* of the angular momentum quantum number, the initial Gaussian basis set already contains functions corresponding to all lower values of this quantum number. Hence, one can assume that the only functions which significantly contribute to the polarization set are those with the angular momentum quantum number higher than the given *l*.

Depending on particular features of the electronic structure of the given atom, one may need to use the polarization approach also for next-to-

valence shells. This happens, *e.g.*, in the case of transition metal elements with exposed next-to-valence d shells which bring a considerable contribution to the overall polarization effect[37,38].

It is worthwhile to note that the contraction coefficients (*13*) in polarization functions will be reduced for orbital exponents $\alpha_\mu > 1$ and will increase for $\alpha_\mu < 1$. This follows nicely the physical picture of the field-induced polarization of the electron density and shows that Gaussian functions with very high exponents can be simply neglected in the expansion (*10*). This observation has led[25,30] to certain empirical rules concerning the reduction of the length of the expansion (*13*).

It is obvious that the success of the method described in this section will also depend on the character of the initial GTO/CGTO set. This initial set must satisfy certain general conditions, appropriate for calculations of atomic dipole polarizabilities and hyperpolarizabilities. One of the important features of the initial Gaussian basis set is that it must be sufficiently diffuse to permit a good description of outer (most polarizable) regions of the electron density distribution. For this reason it is usually worthwhile (if not necessary) to extend standard Gaussian basis sets (*e.g.* of double-zeta quality) by diffuse functions. Such an extension is needed already for the generation of the first-order polarized sets ($p = 1$) for calculations of dipole moments and dipole polarizabilities[25,30] and becomes indispensable in the case of $p > 1$, *i.e.* for the generation of basis sets for calculations of dipole hyperpolarizabilities[39,44,80].

The extension of the initial Gaussian set by diffuse functions is not necessarily highly exposed in the form of atomic valence orbitals; the corresponding expansion coefficients are usually very small and may remain small in contracted polarization functions. The early numerical experiments[25] have shown that to increase the importance of functions with relatively low exponents, one should use atomic eigenvectors obtained in calculations for negative atomic ions. This procedure was devised in the early studies on the generation of polarized basis sets and afterwards systematically used to generate these sets for elements of Groups IVA through VIIA.

It is rather obvious that generating a single contracted polarization function for the given atomic valence orbital may not provide enough flexibility of the polarized basis set. Moreover, in calculations at the correlated levels of approximation, the higher angular momentum functions are also needed to account for the electron correlation contribution to the calculated properties. From this point of view, splitting the given polarization function into the high- and low-exponent parts is quite profitable. Numeri-

cal experiments based on earlier studies by Meyer *et al.*[81–83] have shown that in the case of the first-order polarization functions this splitting significantly improves the calculated values of atomic and molecular electric properties at both SCF HF and correlated levels of approximation.

One should not hesitate to openly say that quite a part of the development of polarized basis sets is based on numerical experiments. The derivation of polarized basis sets for different elements may differ in some details related to certain particular features of the electronic structure of the given atom. The main idea is to obtain from the chosen initial set a contracted "polarized" basis set (target set) of certain assumed size and form. These features are determined pragmatically by requesting some balance between gains (moderately large size of the basis set) and sacrifices (accuracy of the calculated properties). Usually errors in the calculated molecular electric property data of the order of a few per cent are considered to be acceptable. This can be achieved with reasonably small size of the polarized basis sets which permit calculations for quite sizable molecules[84].

In this context one should also stress that the polarized basis sets are developed primarily for *molecular* calculations. The method of their generation is essentially the same for all elements and for this reason the polarized basis sets provide a highly uniform description of the intramolecular polarization of the electron density distribution. However, if used for isolated atoms or atomic ions, the same polarized basis sets may not be particularly successful and their further extension or adaptation may be needed[85].

Initially, the polarized basis sets derived according to the procedure outlined in this section have been devised for nonrelativistic calculations of molecular electric dipole moments and dipole polarizabilities. For heavy systems the same "nonrelativistic" basis sets have been used to estimate relativistic contributions to electric properties in the framework of the perturbation scheme[45,46] based on the Pauli hamiltonian[86]. This approach gives the first-order relativistic correction to electric properties[45,46] and does not need any modification of "nonrelativistic" PolX sets; the relativistic correction to electric properties is totally expressed in terms of nonrelativistic wave functions. Although this first-order method has been found to perform surprisingly well for properties determined primarily by the electronic valence shells[85,87,88], the higher-order relativistic approaches may obviously be needed for other properties[89]. These in turn require relativistic corrections to the wave function whose determination cannot be carried out with basis sets which were strongly contracted at the level of the nonrelativistic approximation[47,87]. For this reason polarized basis sets have been also developed[47,48] for one- and two-component relativistic calculations in the

framework of the Douglas–Kroll approximation[49,51]. Similar "relativistic" basis sets will be presented in this paper for the Group IIIA elements.

GENERATION OF THE FIRST-ORDER POLARIZED BASIS SETS FOR THE GROUP IIIA ELEMENTS

It has already been mentioned that the generation of the first-order polarized basis sets for the Group IIIA elements needs to account for the polarization of both the valence and next-to-valence shells. For $B(^2P)$ the polarization functions for the $1s^2$ shell are automatically supplied by the p subset of the initial atomic basis set. Also, no particular difficulties occur in the case of $Al(^2P)$ since the d polarization set generated according to the usual rules[30] covers the range of the GTO exponents which are important for the subvalence 2p orbital. However, in the case of $Ga(^2P)$, $In(^2P)$, and $Tl(^2P)$, one needs to take into account the polarization of the valence ns and np orbitals as well as the polarization of the subvalence $(n - 1)d^{10}$ shell. Thus, the description of the first-order polarized basis set generation will be given separately for B and Al and for the other three elements.

First-Order Polarized Basis Sets for B and Al

The first-order polarized basis sets for boron and aluminium have been derived earlier[39]. However, for the sake of completeness of this report we will briefly repeat the description of their generation. Moreover, the earlier study of the flexibility of these basis sets was limited to the level of the SCF HF approximation. In the present paper these results will be supplemented by the results of atomic CCSD(T) calculations with restricted open-shell (ROHF) reference functions.

The initial basis set for boron is the energy-optimized (9.5) set of van Duijneveldt[8]. In the first step this basis set was contracted to [9.5/4.2] CGTO set by using 1s, 2s, and 2p SCF ROHF eigenvectors. The contraction in the s subset covers 7 s-type functions with the highest orbital exponents. In the p subset the length of the contraction is limited to 4 p-type functions. In the second step of the basis set generation, the s and p subsets are extended by one diffuse GTO each. The orbital exponents are generated from the assumed geometric progression of orbital exponents in the initial set. The resulting [10.6/5.3] basis set is then used to obtain the SCF ROHF eigenvectors for $B^-(^3P)$.

According to a series of numerical experiments carried out earlier[25], the d-type first-order polarization set can be built from 4 d-type GTOs with or-

bital exponents corresponding to the four lowest exponents in the p subset. This follows immediately from the discussion presented earlier in this paper. Using d-type functions with higher exponents would lead to negligibly small contraction coefficients because of the $\alpha^{-1/2}$ scaling in Eq. (*13*). The single d-type polarization function which would follow from Eq. (*13*) does not have sufficient flexibility to account for both the polarization and electron correlation effects[25]. This observation combined with conclusions of the earlier studies by Meyer *et al.*[81–83] has led to the partition of the single polarization functions into two polarization CGTOs. The first of them comprises the two highest-exponent GTOs, the other one is built of the two lowest-exponent GTOs. This recipe was systematically used to generate first-order polarized basis sets for elements of Groups IVA through VIIA[25,30,32,33,35]. In the present case it results in the first-order polarized basis set of B(^{2}P) of the form [10.6.4/5.3.2]. The basis set details can be read from the PolX basis set library[41,42].

The first-order polarized basis set for relativistic Douglas–Kroll calculations is available as well[53,54]. It differs from the one used in nonrelativistic calculations only by the values of contraction coefficients. These follow from SCF ROHF one-component relativistic calculations with the Douglas–Kroll hamiltonian[47,48,87]. Although the relativistic effects in boron are essentially negligible, for the sake of consistency the use of this basis set is recommended in Douglas–Kroll calculations on molecules containing boron and heavy elements[90].

For Al(^{2}P) the initial basis set is the energy optimized (12.9) GTO basis set of Huzinaga[91]. The generation of the first-order polarized basis set[39] follows the method used for elements of the main Groups IVA–VIIA. The contraction of the initial set to [12.9/6.4] CGTO set was based on 1s, 2s, and 2p SCF ROHF eigenvectors calculated in the uncontracted set. This contraction covers eight highest-exponent GTOs in the s subset and six highest-exponent GTOs in the p subset, leaving the low-exponent GTOs fully uncontracted. It is worthwhile to mention that this way of contracting the initial set leaves uncontracted also a considerable part of GTOs which are important for the description of the 2s and 2p subvalence shells. The [12.9/6.4] is then extended to [13.10/7.5] by the addition of one diffuse s and one diffuse p functions. The extended basis set is used to obtain SCF ROHF eigenvectors for Al$^-$(^{3}P) which determine the d-type polarization functions. The latter are obtained in the same form as for the boron atom, *i.e.*, they are generated from 4 most diffuse p-type GTOs in the form of two CGTOs. In the first of these first-order polarization CGTOs, the orbital coefficients entering Eq. (*13*) are those of the 2p atomic orbital of Al$^-$ and refer

to the fourth and third most diffuse p-type GTO. In the second d-type polarization CGTO, the corresponding coefficients are read from the 3p atomic orbital of Al^- and refer to the second and first most diffuse GTO in the p subset. This way of generating the d-type polarization functions takes care of the possible contribution from the subvalence shell of aluminium. Moreover, the first d-type polarization function is also appropriate for the description of the electron correlation effects in both valence and subvalence shells.

The resulting polarized basis set for aluminium is of the form [13.10.4/7.5.2] and its details are available from the basis set library[41,42]. Its "relativistic" counterpart for Douglas–Kroll calculations is accessible in a similar way[53,54] and is recommended for molecules containing aluminium and heavy elements[92].

First-Order Polarized Basis Sets for Ga, In, and Tl

Starting with Ga the subvalence shell of the Group IIIA elements is of the form $(n - 1)d^{10}$ and the corresponding first-order polarized basis sets should account for its polarization. Hence, according to (*13*), the first-order polarized basis set must also comprise some f-type polarization functions. Since in the case of Al one of the d-type polarization functions was used mostly to describe the polarization effect of the subvalence 2p shell, one can assume that in the case of Ga, In, and Tl, this function will be replaced by its f-type counterpart. The other d-type polarization function will be used to describe the polarization effect in the np valence shell.

The initial primitive GTO basis sets for Ga and In are energy-optimized sets of the form (14.11.5) and (18.14.8), respectively, with orbital exponents determined by Huzinaga[93,94]. The initial GTO set for Tl of the form (19.16.10.5) has been taken from the data of Gropen[9]. In the first step of the generation of the polarized basis sets the initial sets of Ga, In, and Tl have been contracted to [14.11.5/8.6.2], [18.14.8/10.8.4], and [19.16.10.5/12.10.6.2], respectively. The generalized contraction is used mostly for atomic core orbitals; the low-exponent GTOs are essentially left uncontracted and permit high flexibility of the valence and next-to-valence shells of each atom. The contraction coefficients follow from atomic SCF ROHF eigenvectors. The "relativistic" contractions have been determined from atomic DK SCF ROHF eigenvectors.

In the second step of the generation of the first-order polarized sets, the flexibility of the description of the valence and subvalence shells is further increased by adding one diffuse s, p, and d GTOs. The orbital exponents

have been obtained from the continuation of the approximate geometric progression based on two lowest orbital exponents of the initial set. Upon this extension, the basis sets of Ga, In, and Tl become [15.12.6/9.7.3], [19.15.9/11.9.5], and [20.17.11.5/13.11.7.2], respectively. These basis sets have been used in (DK) SCF ROHF calculations for Ga$^-$(^{3}P), In$^-$(^{3}P), and Tl$^-$(^{3}P). The resulting valence np and subvalence (n – 1)d ROHF orbitals have been then employed for the determination of polarization CGTOs.

The f-type polarization functions are assumed to be a linear combination of two GTOs with orbital exponents equal to those of the two most diffuse GTOs of the d subset. The contraction coefficients are determined from the (n – 1)d ROHF eigenvectors of the negative ions according to Eq. (*13*). Similarly, the d-type polarization functions are built as a contraction of two GTOs with orbital exponents equal to those of the two most diffuse GTOs of the p subset. The contraction coefficients follow from the ROHF valence np eigenvectors of the negative ions.

Finally, upon adding the d- and f-type polarization CGTOs, one obtains the first-order polarized basis sets of Ga, In, and Tl of the form [15.12.8.2/9.7.4.1], [19.15.11.2/11.9.6.1], and [20.17.13.7/13.11.8.3], respectively. All basis set details can be found in the basis set library[41,42]. Their "relativistic" counterparts for Douglas–Kroll calculations are also available[53,54]. They differ from the polarized basis sets for nonrelativistic calculations only by contraction coefficients. This difference becomes important already for Ga and using "nonrelativistic" polarized basis sets in relativistic DK calculations may lead to erroneous results.

ATOMIC CALCULATIONS: DIPOLE POLARIZABILITIES

The polarized basis sets are primarily designed for the use in calculations of molecular electric properties. The structure of these basis sets for the Group IIIA elements closely follows that of the polarized basis sets derived earlier for other atoms. Thus, when used in molecular calculations, the basis sets generated in this study are expected to give a well balanced representation of intramolecular polarization effects. It is obvious that these are not the basis sets of choice for atomic calculations of high accuracy. Nevertheless, their performance in calculations of atomic dipole polarizabilities appears to be of some interest. For this purpose we have carried out SCF ROHF and ROHF CCSD(T) [95–98] of the dipole polarizability of the Group IIIA atoms.

All atomic polarizability data presented in this paper correspond to finite field calculations[99–101] with the electric field strength equal to 0.001 a.u. and followed by the finite difference approximation for second derivatives

of energy. The numerical accuracy of the finite difference approximation has been checked at the level of the SCF ROHF method against the first derivatives of the induced dipole moments. The differences between the two sources of the polarizability data are at most of the order of 0.03 a.u. This can be considered as an estimate of the numerical accuracy of our results and is well below inaccuracies resulting from other approximations.

In ROHF CCSD(T) calculations, the number of correlated electrons amounts to 5 for boron (all electrons), 9 for aluminium (frozen $1s^2$ and $2s^2$ shells), and 19 for Ga, In, and Tl ($(n – 1)p^6$, $(n – 1)d^{10}$, ns^2, and np^1 shells are correlated). The subvalence $(n – 1)s^2$ shell in Al, Ga, In, and Tl is systematically kept frozen. The reason is that in relativistic DK calculations, the 4f orbital energy becomes higher than that of the 5s atomic orbitals. Hence, to include the correlation contribution due to $5s^2$ pair, one would have to correlate additionally 14 f-type electrons. This would make the results for Tl to some extent incompatible with those for other atoms. Let us also add that the ROHF CCSD(T) method[95–98] used in this study involves full spin symmetry adaptation.

The nonrelativistic SCF ROHF and ROHF CCSD(T) results for the $M_L = 0$ component of the dipole polarizability of the ^2P state of all atoms considered in this study are presented in Table I. A similar set of the nonrelativistic data for the $M_L = \pm 1$ component is shown in Table II. In both these tables the results obtained with first-order polarized basis sets of this paper are compared with those calculated with the corresponding fully uncontracted basis sets. This comparison shows that for heavier atoms (Ga, In, and Tl) there is a systematic increase in the contraction effect at both the ROHF and correlated levels of approximation. It has been found that this deterioration of the flexibility of the PolX basis sets is primarily due to the contraction of the d-type polarization function. Its decontraction into two primitive GTOs leads to modified first-order polarized basis sets denoted by PolX* whose size is by 5 functions larger than that of the standard PolX sets generated in this study. This, however, removes most of discrepancies between the SCF ROHF results of PolX and fully uncontracted basis sets. Also the agreement between PolX* and uncontracted basis set results obtained at the ROHF CCSD(T) level of approximation is significantly improved. The modified PolX* basis sets are obviously more suitable for atomic calculations than the standard PolX sets. However, these modified sets will not be fully compatible with the PolX bases for other elements and may lead to "overpolarization" effects in molecular calculations.

Analogous results obtained in the relativistic spin-averaged DK approximation with PolX_dk and the corresponding fully uncontracted GTO basis

sets are presented in Tables III and IV. The comparison of the atomic polarizability data calculated with PolX_dk and fully uncontracted GTO basis sets shows essentially the same pattern as that observed in nonrelativistic calculations. Also the decontraction of the d-type polarization function, which leads to modified polarized basis sets PolX_dk*, brings about significant improvement of both SCF ROHF and ROHF CCSD(T) data. In most cases the performance of the PolX_dk* bases is almost as good as that of the corresponding fully uncontracted GTO sets. However, their use in molecular calculations would require that a similar modification is carried out for PolX basis sets for other elements. Otherwise, combining the modified sets derived for the Group IIIA elements with standard polarized basis sets available for other atoms may easily lead to the "overpolarization" effect.

Accurate calculations of electric properties of the isolated atoms should obviously be carried out with large basis sets determined specifically for the given purpose. From this point of view the fully uncontracted basis sets used in our comparative studies appear to satisfy the necessary criteria. It is

TABLE I

The $M_L = 0$ component of the dipole polarizability of the ^2P state of the Group IIIA elements. Nonrelativistic SCF ROHF and ROHF CCSD(T) finite field calculations with the first-order polarized basis sets (PolX), the corresponding fully uncontracted basis sets (GTO), and modified polarized basis sets (PolX*). All data in a.u.

Atom	Method	Basis set[a]		
		PolX	GTO	PolX*
B	ROHF	26.31	26.78	26.75
	CCSD(T)	23.85	23.97	24.54
Al	ROHF	80.15	82.20	82.32
	CCSD(T)	74.31	73.95	76.25
Ga	ROHF	80.59	81.53	81.51
	CCSD(T)	72.98	74.91	74.07
In	ROHF	99.91	102.22	102.20
	CCSD(T)	90.12	94.70	92.71
Tl	ROHF	109.76	112.29	112.19
	CCSD(T)	101.04	104.65	104.78

[a] See text for details of the basis set data.

TABLE II

The $M_L = \pm 1$ component of the dipole polarizability of the ^2P state of the Group IIIA elements. Nonrelativistic SCF ROHF and ROHF CCSD(T) finite field calculations with the first-order polarized basis sets (PolX), the corresponding fully uncontracted basis sets (GTO), and modified polarized basis sets (PolX*). All data in a.u.

Atom	Method	Basis set[a]		
		PolX	GTO	PolX*
B	ROHF	19.17	19.63	19.59
	CCSD(T)	17.90	18.17	18.36
Al	ROHF	51.70	53.22	53.22
	CCSD(T)	47.36	47.93	48.76
Ga	ROHF	46.93	47.69	47.62
	CCSD(T)	40.74	42.44	41.54
In	ROHF	65.05	66.84	66.72
	CCSD(T)	56.07	59.21	57.77
Tl	ROHF	72.06	74.25	74.21
	CCSD(T)	60.93	64.30	63.18

[a] See text for details of the basis set data.

TABLE III

The $M_L = 0$ component of the dipole polarizability of the ^2P state of the Group IIIA elements. Relativistic (DK) SCF ROHF and ROHF CCSD(T) finite field calculations with the first-order polarized basis sets (PolX_dk), the corresponding fully uncontracted basis sets (GTO), and modified polarized basis sets (PolX_dk*). All data in a.u.

Atom	Method	Basis set[a]		
		PolX_dk	GTO	PolX_dk*
B	DK ROHF	26.31	26.77	26.58
	DK CCSD(T)	23.89	23.98	24.38
Al	DK ROHF	80.31	82.54	82.66
	DK CCSD(T)	74.49	74.27	76.59
Ga	DK ROHF	81.99	83.05	83.03
	DK CCSD(T)	74.04	76.02	75.24
In	DK ROHF	102.08	105.00	104.96
	DK CCSD(T)	91.37	96.20	94.37
Tl	DK ROHF	118.22	123.33	123.22
	DK CCSD(T)	110.51	114.19	115.23

[a] See text for details of the basis set data.

worthwhile to recall that their generation involves the extension of the initial basis sets by some diffuse functions and the addition of primitive polarization functions. The latter are derived according to the basis set "polarization" scheme reviewed in this paper. Hence, the corresponding results for atomic polarizabilities presented in Tables I–IV can be considered as the best data calculated so far.

The present atomic GTO calculations have been carried out mostly for the purpose of testing the quality of the PolX and Pol_dk basis sets. However, it appears appropriate to add some general comments on the calculated atomic polarizability values. First, the electron correlation contribution to both components of the ^2P state dipole polarizability of the Group IIIA elements is found to be negative. The contribution of the static relativistic effects becomes visible already for aluminium and increases with the increase of the nuclear charge. Interestingly enough, this contribution is positive for the $M_L = 0$ and negative for the $M_L = \pm 1$ components. Thus, the relativistic effects will significantly increase the absolute values of the dipole polarizability anisotropy of the heavy atoms. Indeed, the polarizability anisotropy,

Table IV

The $M_L = \pm 1$ component of the dipole polarizability of the ^2P state of the Group IIIA elements. Relativistic (DK) SCF ROHF and ROHF CCSD(T) finite field calculations with the first-order polarized basis sets (PolX_dk), the corresponding fully uncontracted basis sets (GTO), and modified polarized basis sets (PolX_dk*). All data in a.u.

Atom	Method	Basis set[a]		
		PolX_dk	GTO	PolX_dk*
B	DK ROHF	19.20	19.62	19.49
	DK CCSD(T)	17.94	18.16	18.38
Al	DK ROHF	51.46	53.11	53.12
	DK CCSD(T)	47.16	47.84	48.68
Ga	DK ROHF	45.70	46.53	46.46
	DK CCSD(T)	39.63	41.36	40.49
In	DK ROHF	59.70	61.81	61.68
	DK CCSD(T)	51.68	54.91	53.65
Tl	DK ROHF	54.25	57.53	57.47
	DK CCSD(T)	47.35	50.48	50.62

[a] See text for details of the basis set data.

$$\Delta\alpha = \alpha(M_L = \pm 1) - \alpha(M_L = 0) \, , \tag{15}$$

calculated for Tl in the nonrelativistic ROHF CCSD(T) approximation with fully uncontracted GTO basis set amounts to –40.35 a.u. (see Tables I and II) whereas the corresponding relativistic DK result is equal to –63.71 a.u. (see Tables III and IV). The anisotropy data for In are equal to –35.49 and –41.29 a.u., respectively. The relativistic effect on the anisotropy of the dipole polarizability of the Group IIIA elements rapidly decreases with the decrease of the nuclear charge. Already for Ga this effect amounts to only –2.19 a.u. and is essentially negligible for aluminium and boron. This pattern of relativistic contributions is accurately reflected by the polarizability data calculated with PolX and PolX_dk basis sets. This observation gives a further support towards the possible use of these basis sets in high-level-correlated calculations of molecular electric properties.

MOLECULAR CALCULATIONS: DIPOLE MOMENTS OF THE GROUP IIIA FLUORIDES

Another test of the performance of the PolX basis sets is carried out by the calculation of dipole moments of the GaF, InF, and TlF. Very accurate nonrelativistic SCF HF multipole moment data for these molecules have been recently calculated by Kobus *et al.*[22] by using the finite difference method for the numerical integration of the HF equations (FD HF)[102–104]. Their dipole moment data will be used as a benchmark for our SCF HF calculations.

All results reported in this section have been calculated at experimental values of the bond distance as used by Kobus *et al.*[22,105] (GaF: 3.353 a.u., InF: 3.752 a.u., TlF: 3.93898 a.u.). In addition to routine SCF HF data, we have also computed the correlated dipole moments by using the RHF CCSD(T) method. The CCSD(T) calculations have been carried out by using the finite field perturbation approach with the external electric field strength equal to ±0.001 a.u. In all CCSD(T) calculations, we have included all valence electrons of fluorine, the $(n-1)p^6(n-1)d^{10}$ subvalence and the valence shell of the Group IIIA element. Hence, our CCSD(T) data correspond to correlating 26 electrons of the outer electronic shells. A similar set of calculations has been carried out in the relativistic spin-averaged DK approximation with PolX_dk basis sets.

The calculated nonrelativistic dipole moment data and the reference values are presented in Table V. The relativistic DK results are given in Table VI. In addition to the results obtained with standard PolX and

TABLE V
Nonrelativistic dipole moments of GaF, InF, and TlF calculated with PolX and PolX* basis sets in SCF HF and CCSD(T) approximations. All values in a.u.

Molecule	Basis set	Method	
		SCF HF[a]	CCSD(T)
GaF	PolX	–0.8841	–0.8988
	PolX*	–0.8837	–0.8961
InF	PolX	–1.1348	–1.1811
	PolX*	–1.1352	–1.1810
TlF	PolX	–1.2981	–1.3917
	PolX*	–1.3006	–1.4018

[a] The benchmark values of the dipole moments of GaF, InF, and TlF from numerical FD HF calculations are –0.8748 a.u., –1.1233 a.u., and –1.2644 a.u., respectively[22]. The conversion factor from Debyes to atomic units is 1 D ≈ 0.39343 a.u.

TABLE VI
Relativistic dipole moments of GaF, InF, and TlF calculated with PolX_dk and PolX_dk* basis sets in DK SCF HF and DK CCSD(T) approximations. All values in a.u.

Molecule	Basis set	Method	
		DK SCF HF	DK CCSD(T)[a]
GaF	PolX_dk	–0.9289	–0.9338
	PolX_dk*	–0.9286	–0.9317
InF	PolX_dk	–1.2650	–1.2800
	PolX_dk*	–1.2652	–1.2802
TlF	PolX_dk	–1.7214	–1.6876
	PolX_dk*	–1.7264	–1.7100

[a] The experimental values of the dipole moments of GaF, InF, and TlF are –0.96 a.u. [106], –1.34 a.u. [106], and –1.650 a.u. [107], respectively. The conversion factor from Debyes to atomic units is 1 D ≈ 0.39343 a.u.

PolX_dk basis sets, we have carried out the same set of calculations with modified PolX* and PolX_dk* basis sets.

As compared to the benchmark FD HF dipole moments of Kobus *et al.*[22], the present SCF HF data are systematically a little too negative. However, these differences are of the order of 1–2% only and seem to be perfectly acceptable in calculations with moderately large basis sets. The modified basis sets (PolX*) of Ga and In lead to essentially the same results as the corresponding PolX sets. However, in the case of TlF, the use of the PolTl* basis set changes the calculated SCF HF dipole moment in the wrong direction, increasing the discrepancy with the numerical FD HF value. This could be considered as a manifestation of the mentioned "overpolarization" effect. In spite of their better performance in atomic polarizability calculations, the modified PolX* basis sets are not recommended in studies of molecular electric properties.

On comparing the nonrelativistic (Table V) and relativistic (Table VI) dipole moments of the three molecules, one finds a marked relativistic effect already in the case of GaF. At the level of the SCF HF approximation, the relativistic effects increase the polarity of this molecule by about 5%. In the case of TlF the relativistic effect accounts for almost 25% of the total DK SCF HF dipole moment. This pattern of the relativistic contribution to the calculated dipole moments is essentially the same in the case of the CCSD(T) data.

The most accurate DK CCSD(T) results of this paper can be compared with the experimental data. For GaF and InF, the experimental values of Hoeft *et al.*[106] correspond to the $v = 0$ vibrational level whereas the calculated values refer to the experimental equilibrium bond distance. Both experimental values are by 3–4% more negative than the present DK CCSD(T) data. The equilibrium value of the dipole moment of TlF (–1.650 a.u.) has been determined by Boeckh *et al.*[107] and is expected to be quite accurate. It agrees with our DK CCSD(T) value (–1.6876 a.u.) within about 2%. All these differences are within the error bars expected for molecular electric properties calculated with PolX and PolX_dk basis sets. Thus, one can conclude that the first-order polarized basis sets derived in this study for the Group IIIA atoms match the quality of basis sets generated earlier for other elements.

As a by-product of our calculations of molecular dipole moments, we have computed the parallel component of the dipole polarizability of GaF, InF, and TlF. The corresponding nonrelativistic and relativistic results calculated with PolX basis sets are presented in Table VII. There seem to be no other data for comparison. One should note that the electron correlation

contribution to the nonrelativistic parallel dipole polarizability is small and positive. The relativistic effects lead to a considerable decrease of the SCF HF polarizability values. The same is observed for the CCSD(T) data. The importance of relativistic effects on the parallel component of the dipole polarizability of GaF, InF, and TlF systematically increases with the increase of the nuclear charge of the heavy atom.

SUMMARY AND CONCLUSIONS

The present study completes the first-order polarized basis sets for elements of the main groups of the Periodic Table. We have surveyed the basis sets available so far, indicating problems which occur in the generation of polarized basis sets for the Group IIIA elements. The principles of what is called the basis set polarization method have been reviewed as well and followed by certain "empirical" rules which lead to well balanced atomic basis sets for the use in high-level-correlated calculations of molecular electric properties. According to these rules, the first-order polarized basis sets have been generated for Ga, In, and Tl to add to the corresponding basis sets derived earlier for B and Al.

Two levels of testing the basis set performance have been investigated. The first was their performance in calculations of the atomic dipole polarizability. The results of calculations with PolX basis sets have been compared with those obtained in calculations with the corresponding fully uncontracted GTO sets. One should mention that the polarization functions in these fully uncontracted sets follow from the same ideas as those used for the derivation of the PolX sets.

TABLE VII
The parallel component of the dipole polarizability of GaF, InF, and TlF. Results of non-relativistic and relativistic calculations with PolX basis sets. All values in a.u.

Molecule	Method			
	SCF HF	DK SCF HF	CCSD(T)	DK CCSD(T)
GaF	32.69	31.95	34.13	33.58
InF	44.73	41.70	46.13	43.84
TlF	49.46	39.52	50.21	43.35

The performance of PolX basis sets in atomic calculations has been found to be satisfactory and confirmed in calculations of the dipole moment of GaF, InF, and TlF. However, to be used in calculations for atoms, the PolX basis sets may need to be modified a little to increase their flexibility in the description of the valence shell polarization effects.

Parallel to investigations in the framework of the nonrelativistic theory, we have developed basis sets (PolX_dk) for spin-averaged relativistic calculations in the DK approximation. These basis sets comprise the same set of primitive GTOs as the PolX bases. They differ, however, by the choice of the contraction coefficients. The pattern of relativistic contributions to electric properties has been studied for atomic dipole polarizabilities and dipole moments and polarizabilities of GaF, InF, and TlF.

One should stress that the first-order polarized basis sets are not designed for the purpose of highly accurate calculations of molecular properties. These basis sets are of moderate size and one must accept certain sacrifices with respect to the accuracy of the calculated data. The goal is to obtain the basic molecular electric properties with the accuracy not worse than a few per cent with respect to available benchmarks and this goal is achieved in most calculations. Obviously, one could further extend the standard PolX and PolX_dk sets to improve upon the computed property data. This would produce polarized basis sets of very high quality and very limited use. One should also stress that the polarized basis sets are for molecular rather than for atomic calculations. Their performance in calculations of atomic electric properties may not be very satisfactory. The PolX and PolX_dk basis sets are definitely purpose- (property-) oriented. They are designed for calculations of basic molecular electric properties and in this particular case they offer certain advantages. They are moderately sized and lead to relatively small errors in high-level-correlated values of molecular dipole moments and polarizabilities.

Finally, one should also remark about the use of polarized basis sets for the study of weak intermolecular interactions[23,108]. Since the polarized basis sets are well saturated for reasonably accurate calculations of molecular dipole moments and dipole polarizabilities, one could expect them to perform quite well in calculations of intermolecular interaction energies. Indeed, as concluded by Chałasiński and Szczęśniak[108], this is generally the case. However, one should bear in mind that the polarized basis sets usually give rather poor monomer energies and the supermolecular approach to the calculation of the interaction energy may be severely affected by the basis set superposition error[109,110]. On the other hand, the usual counterpoise

correction[109] appears to work reasonably well[108], most likely owing to small values of the secondary basis set superposition error[111].

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