

ELECTRIC-FIELD-VARIANT ORBITALS***

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The functional basis sets explicitly depending on the external electric field strength are considered and their usefulness for the calculation of atomic and molecular electric properties is discussed. The concept of the so-called electric-field-variant Gaussian-type orbitals (EFV GTO's) is reconsidered and a particular attention is paid to some specific computational problems arising in the numerical perturbation approach.

The concept of electric-field-variant Gaussian bases is extended to the Slater-type orbitals by using their Gaussian integral transform. The effectiveness of the electric-field-dependent Slater-type bases is illustrated by the polarizability calculations for two-electron atomic systems. Also their superiority in comparison with the EFV GTO's is indicated. It follows from the present paper that the corresponding Slater-type bases should be also quite useful in the calculation of accurate values of molecular electric properties. Additionally, the concept of perturbation-dependent bases is extended for a variety of physically important perturbations.

1. Introduction

It is well known that a reliable theoretical prediction of the so-called atomic and molecular electric properties is usually far more difficult than the calculation of quite accurate energies of isolated atoms and molecules [1, 2]. For rather obvious reasons a vast majority of quantum chemical studies of many-electron systems is energetically oriented. The calculation of sufficiently accurate energy of the isolated many-electron system is usually the main target of these studies. The energy-optimized approximate wave functions may not be appropriate for describing the system response to the external electric field perturbation, i.e., for the calculation of its electric properties. A similar statement is also valid for a number of other atomic and molecular properties [3, 4].

The so-called electric properties of atoms and molecules are precisely defined by subsequent terms in the power series expansion of the electric field dependent energy $E(F)$,

$$E(F) = E^{(0)} + E_{\mu}^{(1)}F_{\mu} + E_{\mu\nu}^{(2)}F_{\mu}F_{\nu} + \dots, \quad (1)$$

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where the repeated Greek subscripts imply the ordinary summation convention and $E^{(0)}$ is the field-free energy of a given system. For F being a static uniform external electric field the first-order term $E_{\mu}^{(1)}$ defines the system dipole moment component

$$\mu_{\mu} = -E_{\mu}^{(1)} \quad (2)$$

and the second-order term $E_{\mu\nu}^{(2)}$ is proportional to the corresponding component of the static electric dipole polarizability

$$\alpha_{\mu\nu} = -2E_{\mu\nu}^{(2)}. \quad (3)$$

These two electric properties of many-electron systems appear to be the most important ones from the experimental point of view. The possibility of a reliable calculation of these properties will not only provide valuable numerical data of unquestionable usefulness but it may also reveal a number of subtleties of the electron density distribution in atoms and molecules.

The standard approach to the calculation of subsequent expansion coefficients of Eq. (1) is by using the appropriate perturbation theory [5]. However, for the perturbation theoretic treatment of the external electric field effects one has to anticipate that the corresponding unperturbed problem has already been solved. In practice this assumption is almost never satisfied and its violation may substantially influence the computed properties [6]. Moreover, to get the second-order term one has to assume that the complete set of eigenfunctions of the unperturbed Hamiltonian is also available. Since all the computational methods of quantum chemistry are naturally limited to finite-dimensional functional spaces, the calculation of other than energy properties of many-electron systems should involve quite extensive, property-directed optimization of trial variation functions.

The task of a full variation optimization of the approximate solution of the perturbation problem can be substantially reduced if a given finite-dimensional set of basis functions depends itself on the external perturbation. This idea of a variable, perturbation-following functional space proved to be extremely useful in the calculation of molecular magnetic properties [4, 7]. The same applies to the so-called floating orbital bases employed for the calculation of molecular forces and force constants [3, 8–10]. In both these cases the perturbation dependence of the basis set functions has usually a fixed analytic form [11, 12] and in fact no additional variation optimization of the variable basis set is required. The success of the corresponding perturbation methods is mainly due to the appropriate, physically justified choice of the perturbation dependence of a given set of functions.

A rather high efficiency of the variable basis set approach in the case of molecular magnetic properties stimulated a search of analogous bases for other classes of physical perturbations. For the external electric field perturbation a set of one-electron basis functions directly depending on the strength of the electric field was first proposed by Moccia [13]. However, Moccia's proposal does not provide enough flexibility of the constructed field dependent set of functions.

Recently, another explicitly field-dependent basis set was suggested by the present author [14] and was shown to be very efficient in the calculation of atomic and molecular electric properties [14–17]. The original proposal was concerned with the so-called Gaussian

functional bases. The aim of the present paper is to extend the concept of the electric-field variant (EFV) Gaussian orbitals to the Slater-type orbital (STO) bases. In the next Section the basis ideas of the EFV Gaussian-type orbital (GTO) bases are briefly reviewed. In Section 3 some computational aspects of perturbation calculations using EFV GTO's are discussed. In the subsequent Section the EFV STO's are introduced by using the Gaussian transform approach and their efficiency is illustrated by several numerical examples. The conclusions concerning the usefulness of the EFV basis sets are summarized in the last section of this paper. Also the possibility of a similar construction of the perturbation-dependent basis sets for other than electric field perturbations, is considered.

2. Electric-field-variant Gaussian-type orbitals

The concept of the EFV GTO basis sets originated from the widespread use of Gaussian functions in molecular calculations [18, 19]. In spite of a rather successful prediction of molecular energies, the standard Gaussian basis sets [20, 21] are known to be quite inefficient in the case of molecular electric properties [9, 22–24]. Naturally, this deficiency of the standard GTO bases can be remedied by the appropriate extension and perturbation-directed selection of the Gaussian orbitals [25]. However, this kind of approach leads immediately to a substantial increase of the overall dimension of the basis set and limits the size of systems which can be considered in this way [23, 24]. Since the total atomic and molecular energy can be computed with a reasonable accuracy using medium-size Gaussian bases, e. g., double-dzeta quality GTO sets [26], it might have been expected that the Gaussian bases of a similar size but explicitly perturbation-dependent should considerably improve the quality of the calculated electric properties.

As already pointed out, the success of variable bases in the case of magnetic field perturbations is mainly due to the appropriate, physically guided choice of the explicit perturbation dependence of the basis functions [4]. Unfortunately, there is nothing like the gauge invariance principle [4] in the case of the external electric field perturbation and in order to devise a reasonable analytic form of the EFV GTO's one should rather consider some inherent features of the Gaussian functions. Each primitive Gaussian orbital can be in principle regarded as an eigenfunction of the harmonic oscillator problem and thus the solution of the corresponding electric field perturbed harmonic oscillator equation is also known. This simple observation was chosen as a basic principle for the construction of the EFV GTO basis set [14].

Suppose that the field-independent problem leading to the zeroth-order energy $E^{(0)}$ was solved in some finite-dimensional Gaussian basis set $\{\chi_1(\mathbf{r}; \mathbf{R}_1, \alpha_1), \chi_2(\mathbf{r}; \mathbf{R}_2, \alpha_2), \dots, \chi_M(\mathbf{r}; \mathbf{R}_M, \alpha_M)\}$ where \mathbf{r} denotes the electron coordinate measured with respect to the i -th GTO origin \mathbf{R}_i and α_i is the corresponding orbital exponent. For each GTO treated as the eigensolution of a separate harmonic oscillator the external electric field \mathbf{F} would introduce the origin shift given by

$$\Delta \mathbf{R}_i = \frac{1}{4\alpha_i^2} \mathbf{F}. \quad (4)$$

In order to account for the differences between a set of independent harmonic oscillators and a given atomic or molecular problem it was proposed [14] to introduce some additional scale factor λ . Thus, the EFV GTO basis set was generated from the original one in the following way

$$\{\chi_i(\mathbf{r}; \mathbf{R}_i(\mathbf{0}), \alpha_i)\} \rightarrow \{\chi_i(\mathbf{r}; \mathbf{R}_i(\mathbf{F}), \alpha_i)\} \quad (5)$$

where

$$\mathbf{R}_i(\mathbf{F}) = \mathbf{R}_i(\mathbf{0}) + \frac{\lambda}{\alpha_i^2} \mathbf{F}. \quad (6)$$

There is a plenty of plausible arguments in favour of the anticipated electric-field dependence of the basis functions. First of all one should notice that the electric field induced distortion of a given orbital is inherently scaled by its exponent. This physically understandable form of the GTO origin shift is expected to play the most important rôle during the field induced deformation of the original basis functions. One can also infer, that the scale factor λ , though possibly different from the harmonic oscillator value of 0.25, should be fairly constant for the GTO bases of similar quality. A more detailed discussion of some important features of the EFV GTO basis sets can be found in Refs. [14, 16].

It is also interesting to compare the present form of the electric field dependent orbitals with that proposed by Moccia [13]. According to Moccia, the field-dependent set is formed from the original one by multiplying each orbital by a common exponential factor of the form $\exp(k\mathbf{r} \cdot \mathbf{F})$, where k is an additional, variationally determined parameter [13]. In contrast to the present form of EVF GTO's, this parameter has to take into account also the differences in the polarization of separate orbitals, i. e., the effects due to different orbital exponents. This is more or less automatically accounted for by Eq. (6). Thus, one can conclude that Moccia's electric field dependent bases will be less flexible than the present ones. This conclusion is further supported by a comparison of the corresponding numerical data presented in Section 5. It is also worth attention that Moccia's proposal represents simply the so-called multiplicative approximation for the perturbed orbitals [27, 28].

The scale factor λ introduced by Eq. (6) can be regarded as a variation parameter which is used to select the most appropriate EFV GTO set from the infinite number of field-dependent sets constructed according to Eqs. (5) and (6). It can be shown [17] that the n -th order perturbed energy $E^{(n)}$ is exactly given by the n -th degree polynomial in λ ,

$$E^{(n)} = e^{(n,0)} + \lambda e^{(n,1)} + \dots + \lambda^n e^{(n,n)}. \quad (7)$$

Thus in even orders of the perturbation theory [29] one can use the minimum condition for Eq. (7) as a source of the best variationally determined value of the scale factor. As regards the choice of the scale factor for odd orders in the perturbation expansion of the field-dependent energy (1) no a priori criterion is available [29].

In the case of second-order perturbed energies Eq. (7) represents a parabolic function of the scale parameter. The corresponding expansion coefficients can be determined either by the analytic differentiation of the total energy formula (1) or by the appropriate finite

difference approach. The latter technique was employed in the calculation of electric dipole polarizabilities and was generally found to be quite satisfactory [15, 16]. However, the use of purely numerical techniques can lead to the violation of some basic assumptions concerning the form of the electric field dependence of the basis set functions. Since the numerical approach seems to be computationally more convenient than the analytic perturbation theory [17] involving the calculation of the first- and second-order derivatives of all molecular integrals, this problem deserves a rather careful consideration. Some remarks concerning a comparison of the so-called analytic approaches to the perturbation theory with purely numerical methods are presented in the next section.

It is also worth attention that the EFV GTO bases considered in the present section were found extremely efficient in the calculation of molecular electric dipole polarizabilities [14–16]. Moreover, if the variationally determined scale factor is assumed to be the same for both the second- and the first-order perturbed energies, a simultaneous improvement of the computed molecular dipole moments is achieved [15, 16]. It is worth attention that only the second-order energy expression of the form (7) provides a possibility of the variation optimization of the scale factor.

According to our previously reported results [14–17] one can conclude that the proposed form of the external electric field dependence of the GTO bases is principally correct and properly accounts for the electric field induced distortion of the electron density distribution in atoms and molecules. This opens the possibility of reliable calculations of atomic and molecular electric properties for quite sizable systems with comparatively small sets of Gaussian basis functions.

3. Some computational aspects of the perturbation theory using perturbation-dependent functions

As already pointed out the scale parameter optimization for the even-order perturbed energies can be carried out either analytically or numerically [17]. The numerical approach, though perhaps less elegant, is undoubtedly more convenient from the computational point of view. The analytic calculation of the expansion coefficients entering Eq. (7) requires the calculation of the derivatives of all molecular integrals up to a given n -th order. Even in the case of the second-order energies this procedure is quite tedious and time consuming [9]. However, at least in the case of the perturbation dependence of the basis set functions as given by Eq. (6) the numerical approach may not be equivalent to the analytic procedure and this question seems to deserve a rather careful consideration¹.

According to what is called here the numerical approach to the field-dependent basis set perturbation theory the total field- and λ -dependent energy $E(\lambda, \mathbf{F})$ is computed at several selected values of the field strength and λ . Then, for each value of λ the appropriate n -th order energy $E^{(n)}(\lambda)$ is calculated using the numerical differentiation of $E(\lambda, \mathbf{F})$ with

¹ The author would like to acknowledge a helpful and stimulating correspondence concerning this problem with Dr. S. T. Epstein.

respect to the field strength. Finally, the n -th order energy (n even) is fitted to the n -th degree polynomial and the best value of the scale parameter λ is determined from the corresponding minimum condition.

In contrast to some other finite-field perturbation approaches [30, 31] the perturbation parameter, i. e., the field strength, enters both the perturbed hamiltonian of a given system and the basis set. Furthermore, the basis set functions depend in fact on the assumed bilinear term λF . This term can be considered as some common variation parameter, say a_μ for the external electric field directed along the μ -th axis of the coordinate system. If this parameter is optimized variationally for the total field dependent energy $E(a_\mu, F_\mu)$, then its power series expansion in terms of F_μ will have in general the following form

$$a_\mu = a_\mu^{(0)} + a_\mu^{(1)}F_\mu + \dots \quad (8)$$

There is no reason that the first term in this expansion should vanish for the unperturbed problem in the case of rather poor GTO basis sets. Nevertheless, its presence will only be manifested in the numerical approach. For the analytic perturbation scheme [17] all coefficients in (8) except for $a_\mu^{(1)} = \lambda$ are *assumed* to vanish. It is practically impossible to introduce this constraint during the numerical determination of the optimal value of the scale factor λ .

Thus, it follows that for the numerical approach it is desirable to check first the field-independent energy of a given system corresponds to the minimum with respect to a_μ treated as a field-independent variation parameter. Otherwise $a_\mu^{(0)}$ may considerably influence the determined value of λ . However, one can expect that for relatively good field independent GTO bases this parameter should be practically negligible. This conclusion follows from the observation that $a_\mu^{(0)}$ will shift the origins of all GTO's in the same direction and therefore is rather unlikely to produce a considerable energy gain. Furthermore $a_\mu^{(0)}$ has to vanish in all calculations performed either for centrosymmetric systems or at optimized molecular geometries.

So far only one example of the mentioned difference between the analytic and the numerical approach was encountered during our calculations [32]. The optimized value of λ for the parallel component of the electric dipole polarizability of HCN computed using 4-31G basis set [33] and experimental molecular energy turned out to be quite large and negative [32]. This result was not only completely different from the optimized λ values computed for a number of other molecules [14-16] but also apparently contradicted the physical picture [14] attached to the meaning of the orbital origin shift (6) induced by the external electric field directed along the molecular axis. On checking the field-independent problem against the minimum with respect to a_μ it was found that $a_\mu^{(0)}$ is considerably different for its zeroth value assumed in the analytic approach. The repeated calculations of the polarizability tensor of HCN with $a_\mu^{(0)}$ included already in the unperturbed GTO basis set went smoothly and led to a small positive value of the optimized scale factor λ .

This example, though hopefully rather exceptional, shows that the perturbation calculations using the EFV GTO bases of relatively poor quality should be performed with some care. It should be also pointed out that a similar feature of perturbation calculations

using external field dependent bases was observed by Eaves and Epstein [34, 35]. Moreover, the same kind of numerical instabilities may also occur in the case of the electric-field-variant STO bases discussed in the next section.

4. Electric-field-variant Slater-type orbitals

In spite of the overwhelming popularity of the Gaussian basis sets the Slater-type orbitals are still frequently in use in both atomic and molecular calculations. The STO bases are known to be considerably more efficient than the GTO functions. Thus a much shorter STO expansion can provide substantially better approximation to the energy of a given system. The perturbation calculations using ordinary STO (field-independent) basis sets suffer from the incompleteness of finite dimensional functional spaces in the same way as in the case of the GTO bases [1]. For instance, the polarizability of the water molecule calculated by using the perturbed self-consistent field (SCF) approach and relatively large STO basis set [36] is only slightly better than that obtained within similar calculations employing GTO's [22]. Both they are considerably different from the expected Hartree-Fock limit [25]. Thus, an explicit introduction of the external electric field dependence into the STO bases can be as useful as in the case of the GTO basis sets. It is also worth attention that for very small GTO bases the EFV GTO technique may not be as efficient as for the corresponding field-variant STO's.²

In principle the field-induced distortion of STO's can be guessed from the exact solutions for the hydrogen atom embedded in the external static homogeneous electric field [37]. However, this approach will not introduce in a natural way any additional variation parameter like the scale factor λ appearing in the definition of the EFV GTO's. The presence of this variation parameter in the EFV GTO bases was found to be very useful and the same can be expected for the EFV STO basis sets. Obviously, the choice of the variable basis set guided by the corresponding solutions for the hydrogen atom will result in the accurate values of electric properties for one-electron atomic systems. However, the missing possibility of an additional optimization of a given variable basis set is not the most convenient feature in the case of many-electron systems. Furthermore, using the hydrogen-like electric field dependent orbitals will practically limit the corresponding perturbation schemes to the consideration of one-centre problems.

The approach we are going to introduce in the present paper is based on the possibility of the so-called Gaussian transform representation of STO's [38]. Any STO can be easily derived [39] from the following integral transform of its exponential part

$$\exp(-\zeta|\mathbf{r}-\mathbf{R}|) = \frac{\zeta}{2\sqrt{\pi}} \int_0^{\infty} s^{-3/2} \exp\left(-\frac{\zeta^2}{4s}\right) \exp(-s|\mathbf{r}-\mathbf{R}|^2) ds \quad (9)$$

² For instance, a single optimized GTO approximation for the 1s orbital of the hydrogen atom [20] does not lead to the quadratic λ -dependence of the EFV GTO polarizability. Because of some intrinsic cancellations in the field-dependent energy expression obtained with a single EFV GTO, the resulting counterpart of Eq. (7) for the hydrogen atom polarizability is linear in λ .

where ζ denotes the orbital exponent and \mathbf{R} is, as previously, the orbital origin position. It follows from Eq. (9) that each STO can be expanded into an infinite series of Gaussians. Thus, for each GTO under the integral sign one can use the same assumptions which led to the EFV GTO bases.

According to this proposal the electric-field-variant STO basis set can be derived from a given field-independent set by using the following field-dependent function

$$f(\mathbf{r}; \mathbf{R}(\mathbf{F}), \zeta) = \frac{\zeta}{2\sqrt{\pi}} \int_0^{\infty} s^{-3/2} \exp\left(-\frac{\zeta^2}{4s}\right) \exp(-s|\mathbf{r} - \mathbf{R}(\mathbf{F})|^2) ds \quad (10)$$

where $\mathbf{R}(\mathbf{F})$ is given by

$$\mathbf{R}(\mathbf{F}) = \mathbf{R}(\mathbf{0}) + \frac{\lambda}{s^2} \mathbf{F} \quad (11)$$

and the scale parameter λ has the same meaning as for the EFV GTO's. Since Eq. (10) is based on our previous experience with the variable Gaussian bases, a major part of the former discussion [14–17] and additional remarks presented in Section 2 of this paper are directly applicable in the case of the EFV STO's. Thus, the field-variant STO's derived according to Eq. (10) correspond to the same picture of the perturbation effects exerted on the original basis set. The EFV STO's are also weighted by the appropriate Gaussian exponents and the scale parameter λ should merely reflect the differences between the exact hamiltonian of a given system and its projected part [40] corresponding to some approximate wave function. Moreover, one should observe that the Gaussian transform representation of EFV STO's (10) indirectly accounts for the effect of GTO's with low orbital exponents. These orbitals were found rather important in our previous study [16] and the available finite Gaussian expansions of STO's [33, 41] usually do not possess this significant feature.

The accuracy of the EFV STO perturbation approach can be easily checked by the calculation of the hydrogen atom polarizability. For the ground state perturbation the second-order energy as a function of the scale parameter λ is given by

$$E^{(2)}(\lambda) = 88\lambda^2 - 28\lambda \quad (12)$$

and its minimum value equals -2.2273 a. u. being very close to the exact value of -2.25 a. u. [42]. On expanding the field-dependent $1s$ hydrogen orbital into a power series in the external field strength one can obtain the explicit formulae for the n -th order perturbed orbitals. All of them are naturally different from the corresponding exact solutions of the perturbation theory equations. However, due to the presence of the variation parameter λ these differences are relatively unimportant for the perturbed energies.

The present example clearly verifies the correctness of our assumptions concerning the analytic form of the EFV STO's. Some further numerical illustration of the applicability of these orbitals to the calculation of atomic dipole polarizabilities within the so-called coupled Hartree-Fock (CHF) perturbation theory [43–45] is given in the next section.

5. Static dipole polarizabilities of two-electron atomic systems using EFV STO's

The results reported in this section refer to the one-electron approximation for many electron systems. At this level the corresponding exact formulation of the perturbation theory is known as the coupled Hartree-Fock approach. The CHF perturbation theory provides the Hartree-Fock accuracy of the computed perturbed energies in the so-called Hartree-Fock limit of the unperturbed problem solution.

In the case of variable basis sets the CHF scheme needs some extension [3, 4]. Recently, a useful density matrix formulation of the CHF perturbation theory has been given [17] and the formulae derived in this paper are utilized in the present case. For two-electron atomic systems considered in this section the corresponding second-order energy formula can be simplified to

$$E^{(2)}(\lambda) = 2 \text{Tr} \{ f^{(2)} - h^{(0)} R^{(0)} S^{(2)} + \frac{1}{2} G(R^{(0)}, g^{(2)}) \} R^{(0)} \quad (13)$$

where for the external electric field $F = (0, 0, F)$ applied along the z axis and the EFV STO basis set $\{\chi_1(F), \chi_2(F), \dots, \chi_M(F)\}$ the matrices entering Eq. (13) are defined by

$$S_{\alpha\beta}^{(2)} = \frac{\partial^2}{\partial F^2} \langle \chi_\alpha(F) | \chi_\beta(F) \rangle \quad (14)$$

$$f_{\alpha\beta}^{(2)} = \frac{\partial^2}{\partial F^2} \langle \chi_\alpha(F) | -\frac{1}{2} \Delta - \frac{Z}{r} - Fz | \chi_\beta(F) \rangle \quad (15)$$

$$g_{\alpha\beta,\mu\nu}^{(2)} = \frac{\partial^2}{\partial F^2} \{ 2 \langle \chi_\alpha(1; F) \chi_\beta(1; F) | r_{12}^{-1} | \chi_\mu(2; F) \chi_\nu(2; F) \rangle - \langle \chi_\alpha(1; F) \chi_\nu(2; F) | r_{12}^{-1} | \chi_\mu(2; F) \chi_\beta(1; F) \rangle \} \quad (16)$$

$$G(R^{(0)}, g^{(2)})_{\alpha\beta} = \sum_\mu \sum_\nu R_{\mu\nu}^{(0)} g_{\alpha\beta,\mu\nu}^{(2)} \quad (17)$$

and

$$h_{\alpha\beta}^{(0)} = \langle \chi_\alpha(0) | -\frac{1}{2} \Delta - \frac{Z}{r} | \chi_\beta(0) \rangle \quad (18)$$

$R^{(0)}$ is the density operator representation in the unperturbed basis set $\{\chi_\alpha(0)\}$ and Z denotes the nuclear charge. In comparison with a rather complicated general second-order energy formula [17] the present simplification is merely achieved by a natural limitation of the unperturbed basis set to s -type STO's. It should be also pointed out that all derivatives given by Eqs. (14)–(16) implicitly depend on the scale factor λ through the EFV STO basis functions.

In order to check the relative effectiveness of the EFV STO perturbation approach a series of the helium atom polarizability calculations was performed using the SCF wave functions of different accuracy. The results of these calculations are shown in Table I together with our previous data obtained using the corresponding EFV GTO's [17].

TABLE I

Helium atom polarizability calculations using electric-field-variant orbital bases. (all entries in a. u.)

EFV STO basis set ^a				EFV GTO basis set ^b			
Basis set dimension <i>M</i>	Unperturbed SCF energy $E_{\text{SCF}}^{(0)}$	Polarizability α	Optimized value of λ	Basis set dimension <i>M</i>	Unperturbed SCF energy $E_{\text{SCF}}^{(0)}$	Polarizability α	Optimized value of λ
1	-2.8476563	1.1226	0.1626	2	-2.747066	0.8834	0.1752
2	-2.8616700	1.3210	0.1351	3	-2.835680	1.0886	0.1585
4	-2.8616785	1.3193	0.1332	5	-2.859896	1.2720	0.1428
5	-2.8616799	1.3212	0.1340	8	-2.861625	1.3177	0.1360
				10	-2.861673	1.3214	0.1348
HF limit	-2.8616800	1.32 ^c	—				

^a Basis set functions and SCF orbitals taken from Ref. [46]. ^b Taken from Ref. [17]. ^c Taken from Ref. [48].

For the sake of a simultaneous comparison of the accuracy of the zeroth-order SCF wave functions and its influence on the calculated polarizability values also the unperturbed SCF energies $E_{\text{SCF}}^{(0)}$ are included in Table I. The present results clearly indicate that the EFV STO bases are far more effective than the EFV GTO bases. This observation corresponds to a much faster convergence of the STO expansions for the unperturbed system than in the case of GTO's. It is worth attention that the result for 2 EFV STO basis set is practically as good as that obtained previously with 10 EFV GTO's. Thus, although the integrals involving STO's are generally more difficult than those for the GTO basis sets, the EFV STO bases of a comparable quality are much shorter. This fact may define the usefulness of the EFV STO basis sets in the calculation of molecular electric properties.

TABLE II

Polarizabilities of two-electron atomic systems (in a. u.)

Atom or ion	EFV STO results ^a		Reference CHF results ^b
	α	Optimized λ	
He	1.3193	0.1332	1.3227
Li ⁺	0.1889	0.1424	0.1896
Be ²⁺	0.0514	0.1453	0.0519
B ³⁺	0.0192	0.1423	0.0196
C ⁴⁺	0.0089	0.1502	0.0089
N ⁵⁺	0.0046	0.1516	0.0046

^a All EFV STO calculations correspond to the 4 STO basis set of Clementi [46]. ^b Taken from Ref. [47].

A further illustration of the efficiency of the EFV STO bases is given by the data of Table II. In this Table the results of present calculation using basis set of 4 *s*-type Slater orbitals [46] are compared with near-Hartree-Fock CHF data of Epstein and Johnson [47]. For the considered series of two-electron systems He, Li⁺, Be²⁺, B³⁺, C⁴⁺ and N⁵⁺ the present results obtained using the EFV STO CHF approach accompanied by the optimization of the variation parameter λ also represent near-HF accuracy.

It should be also pointed out that the optimized value of the scale parameter λ is fairly independent of both the basis set quality and the nuclear charge. A similar behaviour of λ has already been noticed for the EFV GTO bases [14-16], though the corresponding numerical values of this parameter were generally smaller than in the present case [15, 16].

Finally, our results for the helium atom polarizability can be compared with the calculations by Moccia [13]. The polarizability value obtained by Moccia $\alpha_{\text{He}} = -2E^{(2)} = 1.1$ a. u. was calculated using the EFV STO basis set of 3 *s*-type functions. The electric field, according to Moccia's proposal [13] was included by multiplying each orbital by the exponential factor $\exp(kF \cdot r)$. According to the data of Table I Moccia's value roughly corresponds to our calculations with minimum STO basis set and is substantially smaller than the expected HF limit. Using the basis set of 2 STO's within the present approach one already reaches quite satisfactory accuracy of the computed He atom polarizability. Thus, the form of the electric field dependence of the basis set functions introduced by Moccia [13] does not seem to be especially efficient.

6. Conclusions. Some proposals concerning variable bases for the calculation of atomic and molecular properties

The results presented in the previous section clearly show that the EFV STO bases should be generally much more efficient than the corresponding GTO sets. The use of the EFV STO functions for atomic systems does not represent any substantial difficulty since all the required integrals can be done analytically. However, the atomic systems are not as interesting as molecules. In fact there is a plenty of numerical data for the polarizability of atoms and ions and the present calculations do not provide new numerical values in this respect. The main reason for these calculations was to exemplify the effectiveness of the proposed field-dependent basis set. The most significant feature of the EFV STO bases would be their relatively easy implementation in molecular calculations.

As already pointed out, the EFV STO bases providing a reasonable accuracy of the computed atomic polarizabilities are much shorter than the corresponding EFV GTO bases. For many-electron system the reduction of the basis set dimension by a factor of 5 (see Table I) would mean that the number of two-electron integrals to be computed is roughly reduced by a factor of 5⁴. This is a rather substantial gain even if the integrals over STO's are much more difficult than the integrals involving GTO's. Moreover, the use of the Gaussian transform technique [38, 39] which is completely natural in the case of the proposed form of EFV STO's (10), should considerably facilitate the calculation of molecular integrals. One can therefore conclude that the calculations using the EFV STO basis sets are completely within the reach of the present-day computational techniques

and facilities. Similarly as in the case of the EFV GTO bases the corresponding calculations can be performed either completely numerically or by using the so-called analytic approach. There is also a possibility of a mixed computational scheme [17].

Let us also notice that the proposed EFV STO approach can be very useful in the calculation of the correlation corrections to atomic electric properties. Another possible application of EFV STO's can be the calculation of higher order atomic polarizabilities. The EFV GTO calculations of the second-order hyperpolarizability of He [17] proved to be quite successful and even better results can be expected for the EFV STO basis set.

A considerable success and efficiency of the EFV GTO and STO bases in the calculation of atomic and molecular electric properties should stimulate a search for other perturbation-dependent bases with the explicit perturbation-dependence following from similar considerations. Let us point out that the perturbed harmonic oscillator equation can be exactly solved for a number of interesting perturbation operators. Among them one should pay a rather particular attention to x_μ^2 -type terms. These operators will correspond for instance to the quadrupole field perturbation or to the perturbation by the external magnetic field. Including their effect in the basis set would mean a change of the orbital exponents. Introducing the appropriate variable bases could facilitate the calculation of quite accurate values of electric quadrupole polarizabilities or diamagnetic susceptibilities. In the latter case the external magnetic field dependence of the basis set functions is also partly accounted for by the so-called gauge factors. These, however, lead merely to the improvement of the paramagnetic part of the susceptibility tensor [4].

One can conclude that the approach discussed in the present paper for the electric field perturbation can be easily extended for several other problems. The most important feature of the variable basis set methods is that they provide a very efficient way of circumventing the incompleteness problems in perturbation calculations of atomic and molecular properties.

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