Vol. A57 (1980) *ACTA PHYSICA POLONICA* No 6

ELECTRIC–FIELD–VARIANT ORBITALS.
IV. ATOMIC QUADRUPOLE SHIELDING FACTORS*

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(Received December 17, 1979)

The accuracy of the electric-field-variant (EFV) basis sets generated previously for the calculation of atomic quadrupole polarizabilities is checked by computing the quadrupole shielding factors. By virtue of the form of the quadrupole shielding perturbation operator the present calculations provide a check on the quality of the EFV bases at short electron-nucleus distances. The EFV results obtained for the quadrupole shielding factors of 2- and 4-electron atomic systems are close to the most accurate coupled Hartree–Fock data. This is achieved by using a single parameter whose numerical value is fixed during the variation calculation of the quadrupole polarizability. The present results indicate that the EFV bases provide a reliable description of both the inner and the outer regions of the perturbed electron density distribution.

1. *Introduction*

The generation of the EFV basis sets which has been discussed in previous parts of this series [1–3] is based on the consideration of the external electric field perturbation [1, 2, 4]. Since the field-modified bases are by no means complete, they can be optimized with respect to the properties which are to be computed. In the case of the external electric field gradient perturbation this optimization is carried out with regard to the diagonal elements of the quadrupole polarizability tensor [2]. The corresponding perturbation operator [2, 3, 5] weights heavily the outer regions of the electron density distribution and the EFV bases determined in this way may not be appropriate for the calculation of other second-order properties related to the same perturbation.

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* This work was partly supported by the Institute of Low Temperatures and Structure Research of the Polish Academy of Sciences under contract No. MR-I.9.4.3/2.

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A very convenient check on the accuracy of the first-order perturbed wave functions resulting from the multipole moment perturbation is provided by the quantity known as the multipole shielding factor [6, 7]. The m-th component of the 2^l-pole shielding perturbation operator $\hat{f}^{(0,1)}_{l,m}(i)$ for the i-th electron is given by

$$\hat{f}^{(0,1)}_{l,m}(i) = r_i^{-2l-1}\hat{Q}_{l,m}(i), \qquad m = -l, -l+1, \ldots, l-1, l, \tag{1}$$

where $\hat{Q}_{l,m}(i)$ is the m-th component of the 2^l-pole moment operator. In comparison with the i-th electron 2^l-pole moment perturbation operator

$$\hat{f}^{(1,0)}_{l,m}(i) = -\hat{Q}_{l,m}(i) \tag{2}$$

which defines the 2^l-pole polarizability tensor [7], the operator (1) is large in the neighbourhood of the atomic nucleus.

For a spherically symmetric system the rotational average of the 2^l-pole shielding factor tensor can be defined as [7]

$$\beta_l = 2\langle \Psi^{(1,0)}_{l,0}| \sum_i \hat{f}^{(0,1)}_{l,0}(i)\, |\Psi^{(0)}\rangle \tag{3}$$

and involves the first-order perturbed wave function $\Psi^{(1,0)}_{l,0}$ determined for the perturbation $\sum_i \hat{f}^{(1,0)}_{l,0}(i)$. Alternatively, one can also write

$$\beta_l = 2\langle \Psi^{(0,1)}_{l,0}| \sum_i \hat{f}^{(1,0)}_{l,0}(i)\, |\Psi^{(0)}\rangle, \tag{4}$$

where $\Psi^{(0,1)}_{l,0}$ is the first-order perturbed function for the corresponding component of the 2^l-pole shielding perturbation. The equivalence of both these definitions of β_l follows immediately from the so-called interchange theorem [8] provided the perturbed functions are either exact or expanded in the same set of other functions [9]. In most cases, however, the set of expansion functions is determined via the 2^l-pole polarizability calculation [10]. Then, if β_l is computed according to Eq. (3) its accuracy will reflect the accuracy and flexibilityof variationally determined first-order perturbed function $\Psi^{(1,0)}_{l,0}$.

In the present paper the quadrupole shielding factors β_l will be calculated for a series of two- and four-electron atomic systems. We shall employ the first-order perturbed SCF functions obtained in our recent calculations of the corresponding quadrupole polarizabilities [2, 3]. The computed values of β_l will be then compared with the most accurate SCF results reported in the literature. This comparison will be used to assess the quality of the perturbed SCF EFV GTO and SCF EFV STO functions which follow from the optimization of the atomic quadrupole polarizabilities.

2. *The method of calculation*

All calculations reported in this paper refer to the SCF HF approximation and involve the SCF perturbation theory for perturbation-dependent non-orthogonal bases [11]. The EFV bases which depend explicitly on the external electric field gradient are generated from a given finite set of atomic functions $\{\chi_1(\mathbf{r}; \mathbf{a}_1(0)), \chi_2(\mathbf{r}; \mathbf{a}_2(0)), \ldots, \chi_m(\mathbf{r}; \mathbf{a}_m(0))\}$ which is used to describe the unperturbed system. The dependence on the field gradient strength $V = V_{2,0}$ is introduced through a modification of the orbital exponent tensor $\boldsymbol{a}_i$ for each primitive function of the initial basis set [2, 3]. In the case of the GTO bases the analytic form of this modification follows directly from the consideration of appropriately perturbed harmonic ascillator [2]. The generation of the EFV STO bases involves additionally some integral transform representation of the exponential part of STO's [3]. In order to make the V-dependent sets more flexible some variation parameter λ has been introduced [2, 3] and optimized via the minimization of the second-order energy $E_{2,0}^{(2,0)}$ resulting from the perturbation $\hat{f}_{2,0}^{(1,0)}$. The final EFV bases can be written as $\{\chi_i(\boldsymbol{r}; \boldsymbol{a}_i(V, \hat{\lambda}))\}_m$ where $\hat{\lambda}$ denotes the optimized value of the parameter λ and m is the basis set dimension. It is important to stress that the value of m is the same for both the unperturbed and the perturbed problem.

Since the EFV bases derived in this way depend only on the strength of the $\hat{f}_{2,0}^{(1,0)}$ perturbation the general formula for the mixed second-order energy $E_{2,0}^{(1,1)} = \beta_2$ (see Eq. (38) of Ref. [11]) simplified to

$$\beta_2 = E_{2,0}^{(1,1)} = 2\,\mathrm{Tr}\,\{\boldsymbol{f}_{2,0}^{(1,1)}\boldsymbol{R}^{(0)} + \boldsymbol{f}_{2,0}^{(0,1)}\boldsymbol{R}_{2,0}^{(1,0)}\}, \tag{5}$$

where

$$\{f_{2,0}^{(1,1)}\}_{ij} = \left\langle \left(\frac{\partial \chi_i(V, \hat{\lambda})}{\partial V}\right)_{V=0} \middle| \hat{f}_{2,0}^{(0,1)} \middle| \chi_j(0, 0) \right\rangle + \left\langle \chi_i(0, 0) \middle| \hat{f}_{2,0}^{(0,1)} \middle| \left(\frac{\partial \chi_j(V, \hat{\lambda})}{\partial V}\right)_{V=0} \right\rangle, \tag{6}$$

$$\{f_{2,0}^{(0,1)}\}_{ij} = \langle \chi_i(0, 0) | \hat{f}_{2,0}^{(0,1)} | \chi_j(0, 0) \rangle, \tag{7}$$

$$\chi_i(0, 0) = \chi_i(\boldsymbol{r}; \boldsymbol{a}_i(0, 0)),$$

and $\boldsymbol{R}^{(0)}$ and $\boldsymbol{R}_{2,0}^{(1,0)}$ are the unperturbed and the first-order perturbed density matrices, respectively [11]. Furthermore, in the case of the two- and four-electron atomic systems considered in the present paper the unperturbed bases will involve solely the s-type functions. Thus, for symmetry reasons, one has

$$\boldsymbol{R}_{2,0}^{(1,0)} = \boldsymbol{0}, \tag{8}$$

and

$$\beta_2 = 2\,\mathrm{Tr}\,\boldsymbol{f}_{2,0}^{(1,1)}\boldsymbol{R}^{(0)}. \tag{9}$$

According to the assumed analytic form of the EFV functions the derivatives which enter Eq. (6) are linear in $\hat{\lambda}$, and therefore the calculated shielding factors will also linearly depend on this parameter. In this way $\beta_2 = \beta_2(\hat{\lambda})$ is intimately related to the quality of the EFV results for the quadrupole polarizability of a given system. Once the value of $\hat{\lambda}$ is known, the calculation of $\beta_2(\hat{\lambda})$ becomes relatively straightforward.

3. *Results and discussion*

We shall first discuss the results obtained by using the GTO basis sets. The corresponding calculations have been performed for a series of different GTO bases and enabled us to study the m-dependence of β_2. The initial V-independent GTO functions have been taken from van Duijneveldt's Report [12]. The corresponding values of $\hat{\lambda}$ have already been given in Part II of this series [2]. The calculations of β_2 have been carried out for

H, He and Be. Also the hydrogen atom[1] has been included in this series, for it makes possible a comparison of the EFV GTO data with the exact value of β_2 which is equal to $\frac{1}{3}$.[7].

The results of our EFV GTO calculations are shown in Table I. It should be pointed out that if the GTO bases were not perturbation dependent, the results for β_2 would be exactly equal to zero, since there are no V-independent GTO's of appropriate symmetry. Thus, our result obtained for the hydrogen atom by using the largest 10s EFV GTO set, though it differs by ca. 10 per cent from the exact value of β_2, should be considered as fairly satisfactory. According to the data presented in Table II a similar conclusion applies also to our results for He and Be. The EFV GTO data for the largest basis sets are not too different from the corresponding accurate CHF values [13, 14]. The existing discrepancies will be considered on discussing the EFV STO results.

TABLE I

Quadrupole shielding factors for H, He and Be by using the EFV GTO bases. The convergence study

Basis set dimension (m)	Quadrupole shielding factor (β_2)[a]		
	H	He	Be
2	0.3769	0.4737	1.0933
3	0.3500	0.4476	1.1175
4	0.3312	0.4252	1.1347
5	0.3181	0.4075	1.1425
6	0.3102	0.3944	0.9999
7	0.3045	0.3860	0.9701
8	0.3019	0.3803	0.9658
9	0.2993	0.3759	0.9675
10	0.2985	0.3738	0.9412
11			0.9117
12			0.9107
13			0.9117

[a] The original GTO bases taken from van Duijneveldt's Report [12]. All entries refer to the corresponding optimized values of the parameter λ as given in Ref. [2]. See Text for details.

The dependence of β_2 on the basis set size has a perfect monotonic behaviour for H and He and follows that observed in the case of quadrupole polarizabilities [2]. It can be seen from the data of Table I that presumably a little can be gained by a further increase of the basis set size. Some non-monotonic variation of β_2 for Be appears to have its origin in incomplete optimization of the corresponding initial GTO bases [2]. The same has already been observed in our calculations of the quadrupole polarizability of Be [2].

On employing the EFV GTO bases the accuracy of β_2 can be affected by the following two factors: (*i*) the inaccuracy of the first-order perturbed wave function, and (*ii*) the inaccuracy of the unperturbed wave function. By the form of the perturbation operator $\hat{f}^{(0,1)}$ one can expect that the accuracy of both functions in the neighbourhood of the nucleus can be of principal importance. However, it is known [15] that the GTO's can hardly

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[1] For one-electron systems the factor 2 in front of the trace in Eq. (9) should be omitted.

TABLE II

Quadrupole shielding factors. A comparison of the EFV results with the best literature data

Atom or ion	This work[a]		Exact or accurate CHF values
	EFV GTO[b]	EFV STO[c]	
H	0.299	0.296	0.3333 [7][d]
He	0.374	0.368	0.388 [13], 0.396 [14]
Li^+		0.225	0.248
Be^{2+}		0.158	
B^{3+}		0.125	
C^{4+}		0.104	
Be	0.912	0.779	0.77 [13]
B^+		0.528	0.55 [13]
C^{2+}		0.430	0.43 [13]

[a] Calculated for the optimized values of the parameter λ as reported in Refs. [2, 3].

[b] The corresponding entries refer to the largest EFV GTO bases employed in the present paper. See Table I for details. The GTO bases with optimized orbital exponents are not available for the ionic systems.

[c] Exact zeroth-order function for H, 5 STO basis set for He, 4 STO bases for Li^+ through C^{4+}, 6 STO basis set for Be, and 5 STO bases for B^+ and C^{2+}. The original STO bases taken from Clementi's Tables [16].

[d] Exact result.

simulate the so-called nuclear cusp condition and this seems to be one of the most important reasons for the observed discrepancies. From this point of view the STO bases ars far more appropriate. Thus, on using the EFV STO functions [3] one can almost eliminate the effect of the inaccuracy of the zeroth-order solution.

The results of our EFV STO calculations for a series of two- and four-electron atoms and ions are reported in Table II. The initial STO bases have been taken from Clementi's Tables [16] and the appropriate values of λ have been determined in Part III of this series [3]. One should notice that in the case of the hydrogen atom the EFV STO result corresponds to the exact zeroth-order function and in this way provides a measure of the accuracy of the first-order perturbed EFV STO function. The discrepancy between the exact and the EFV STO value of β_2 amounts in this case to ca. 10 per cent, being similar to that observed for the 10s EFV GTO set. However, far better results are obtained for the He and Be isoelectronic series. The present values of β_2 are only slightly different from the best CHF data calculated by using the ordinary expansion techniques [13].

One may wonder why the result for the hydrogen atom is poorer than those for two- and four-electron systems, though in the latter case the finite STO bases give only approximate HF orbitals. In the case of the hydrogen atom, however, the flexibility of the first--order perturbed EFV STO function is diminished by the fact that there is only a single unperturbed orbital. Using several STO's for He- and Be-like systems provides a higher flexibility of the EFV STO approach, though the corresponding zeroth-order orbitals are to some extent inaccurate.

Both the EFV GTO and the EFV STO values of β_2 computed in this paper show that the perturbed functions which follow from the variation of a single parameter λ are also quite reasonable in the region close to the atomic nucleus. According to our previous studies these functions have been shown to give the atomic quadrupole polarizabilities of a very high accuracy [2, 3]. Thus, the present results provide a further confirmation of the usefulness of the EFV bases for the calculation of second-order properties. This conclusion can be of some importance for the calculation of the inhomogeneous electric field effects on molecular properties [17, 18]. The use of EFV bases, for instance, for the calculation of the electric field gradient effects on nuclear magnetic shielding constants may lead to a substantial reduction of the basis set size problem [17, 18].

The main purpose of this paper was to study the quality of the EFV bases at short electron-nucleus distances. It has been shown that fairly reasonable results for β_2 can be obtained without any further modification of previously proposed [2, 3] dependence of the basis set functions on the field gradient strenght. However, in order to obtain very accurate values of β_2 by using the EFV GTO bases some further extension of the method appears to be desirable. The same applies to the EFV STO approach for the hydrogen atom. The easiest extension of the present approach can be obtained by making a given basis set simultaneously dependent on both perturbations. The dependence on the strength of the $\hat{f}_{2,0}^{(0,1)}$ perturbation should involve lower powers of the electron-nucleus distance than the dependence on $\hat{f}_{2,0}^{(1,0)}$. Some pilot calculations performed for the hydrogen atom indicate that by dividing the n-th order term in the expansion of χ_i by r^n one obtains a considerable improvement of β_2. However, the explicit dependence of χ_i on the strength of both perturbations makes all calculations more complicated. This should be rather avoided if the EFV bases are to be applied in molecular problems.

Finally, let us mention that the idea of the EFV bases has originally been introduced [1, 4] for the calculation of atomic and molecular electric dipole polarizabilities. The quantity appropriate for checking the accuracy of these bases is known as the dipole shielding factor [6, 7]. We have also performed similar calculations of the dipole shielding factor for H and two- and four-electron atomic systems. For the hydrogen atom and the He-like series both the EFV GTO and the EFV STO bases give results which are fairly close to the corresponding exact dipole shielding factors [6, 7]. In the case of four-electron systems the EFV values are, however, much poorer. On the other hand they represent a considerable improvement over the dipole shielding factors calculated by using what is known as the multiplicative approximation for the first-order perturbed orbitals [9, 10]. Nonetheless, it appears that the basis set modification obtained for the homogeneous electric field perturbation [1, 4] is less uniform for the whole range of electron-nucleus distances than that deduced for the electric field gradient perturbation [2, 3].

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