ELECTRIC-FIELD-VARIANT ORBITALS
III. EXPLICIT FIELD-GRADIENT DEPENDENCE OF STO'S AND THE CALCULATION OF ATOMIC QUADRUPOLE POLARIZABILITIES*

BY K. WOLIŃSKI

Institute of Chemistry, M. Curie-Skłodowska University, Lublin**

AND A. J. SADLEJ

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw***

The concept of the electric-field-variant (EFV) atomic basis sets is extended for the perturbation by the inhomogeneous electric field with a constant gradient. The functional dependence of the Slater-type orbitals (STO's) on the strength of the field gradient is generated using the approach recently devised for the Gaussian-type orbitals and the appropriate integral transform. The EFV STO's derived in this way are utilized for the calculation of atomic quadrupole polarizabilities. The accuracy of the EFV STO approach is discussed by the comparison of the present results with the accurate quadrupole polarizability of the hydrogen atom. Then the EFV STO method is applied to the calculation of quadrupole polarizabilities of isoelectronic He- and Be-like systems. The latter calculations are performed within the coupled Hartree–Fock scheme and their results indicate a good performance of the method. It is of note that using the EFV STO bases does not require any explicit extension of the basis set for perturbation calculations.

1. Introduction

The interest in multipole polarizabilities is primarily due to their importance for the determination of the so-called induction contribution to the interatomic and intermolecular interaction energies [1, 2]. Of the 2^L-pole polarizabilities only the dipole ($L = 1$) polariza-

---

** Address: Instytut Chemii, Uniwersytet M. Curie-Skłodowskiej, Nowotki 12, 20-031 Lublin, Poland.

*** Address: Instytut Chemii Organicznej PAN, Kasprzaka 44, 01-224 Warszawa 42, Poland.

bility can be directly obtained from the experimental data [1]. The other ones, whose knowledge is required for the calculation of higher-order multipole contributions to the induction energy [2], can only be determined by using the theoretical methods. This, in principle, can be accomplished by means of the perturbation theory [1]. It is worth attention that already in the case of the electric dipole polarizabilities their accurate calculation may represent quite a problem even for relatively small systems [3]. Computing the higher multipole polarizabilities becomes increasingly difficult and the corresponding data are rather scarce.

The approximate nature of quantum mechanical treatment of many electron systems makes the formal perturbation theory equations computationally intractable. Even the Hartree–Fock perturbation theory [4–6], which undoubtedly represents a reasonable choice between the computational effort and the quality of the calculated polarizabilities, suffers from several shortcomings. It is the so-called basis set problem which usually limits the range of applicability of this theory. Shortly speaking, in order to describe properly the system response to the external perturbation one needs far more basis functions than in the calculations for the unperturbed system [7–9]. This makes at least the corresponding perturbation calculations quite expensive, if possible at all.

An alternative solution to the basis set problem in perturbation calculations of atomic and molecular polarizabilities has recently been proposed by one of the present authors [10]. In contrast to standard Hartree–Fock perturbation calculations which involve some specific extension of the basis set [7, 11–13] this new approach employs virtually the same set of functions for both the unperturbed and the perturbed system. However, the set of functions used to describe the perturbed system is explicitly dependent on the external perturbation strength. The corresponding one-electron functions are referred to as the field-variant orbitals.

In Part I of this series [14] the field-variant orbitals for the electric field perturbation, i.e. the so-called electric-field-variant (EFV) orbitals have been considered with respect to their applicability to the calculation of accurate Hartree–Fock (HF) dipole polarizabilities. In addition to the EFV Gaussian-type orbitals (GTO's) [10, 15], whose efficiency in the calculation of molecular dipole polarizabilities is already well established [15–17], also the corresponding Slater-type orbital (STO) basis sets have been proposed. More recently, the concept of the EFV GTO basis sets has been extended for the perturbation by the inhomogeneous electric field with a constant field gradient [18] and applied to the calculation of atomic quadrupole polarizabilities.

In the present paper we shall consider the EFV STO bases for the external field gradient perturbation. They will be introduced by the appropriate integral transform of the EFV GTO functions defined in Part II of this series [18]. The EFV STO bases will be applied to the calculation of atomic quadrupole polarizabilities and their advantages and disadvantages with respect to the corresponding EFV GTO functions will be discussed. The present study is limited to the Hartree–Fock approximation and we shall not enter any detailed discussion of the pertinent correlation effects. However, it should be pointed out that both the EFV GTO and the EFV STO bases can also be utilized in perturbation calculations of the correlation contribution to the multipole polarizabilities [19–21].

2. Electric-field-variant basis sets for the calculation of quadrupole polarizabilities

2.1. The quadrupole polarizability

Before discussing the relevant EFV bases let us summarize the basic concepts and definitions. We assume that the external perturbation is due to a constant field gradient which is defined by five components $V_{2,m}$ ($m = -2, ..., +2$) of the second-rank irreducible tensor V_2 [22]. The components are assumed to be real. Then, the perturbation term in the Hamiltonian of a given many-electron system will have the following form

$$\hat{H}^{(1)} = - \sum_{m=-2}^{+2} \sum_i \hat{Q}_{2,m} V_{2,m}, \tag{1}$$

where $\hat{Q}_{2,m}(i)$ is the m-th component of the i-th electron quadrupole moment operator defined in terms of normalized tesseral harmonics [23]. In the presence of the perturbation (1) the total perturbed energy $E(V_2)$ can be expanded into the power series with respect to the components of V_2, i.e.

$$E(V_2) = E^{(0)} + \sum_{m=-2}^{+2} E_{2,m}^{(1)} V_{2,m} + \sum_{m=-2}^{+2} \sum_{m'=-2}^{+2} E_{2,m;2,m'}^{(2)} V_{2,m} V_{2,m'} + \text{higher-order terms}, \tag{2}$$

where the superscripts refer to the order of the perturbation expansion. On the other hand the empirical expression for the perturbed energy is

$$E(V_2) = E^{(0)} - \sum_{m=-2}^{+2} Q_{2,m} V_{2,m} - \tfrac{1}{2} \sum_{m=-2}^{+2} \sum_{m'=-2}^{+2} \alpha_{2,m;2,m'} V_{2,m} V_{2,m'} + \ldots \tag{3}$$

and thus the components of the quadrupole moment $Q_{2,m}$ can be identified with the negative of the pertinent components of the first-order perturbed energy $E_{2,m}^{(1)}$, while the quadrupole polarizability tensor is defined by

$$\alpha_{2,m;2,m'} = -2E_{2,m;2,m'}^{(2)}. \tag{4}$$

The latter definition is analogous to that employed by Mulder et al. [24]. However, it differs from the definition by Buckingham [1] who defines the quadrupole polarizability tensor in terms of its cartesian components.

For spherically symmetric systems the whole tensor (4) is determined by a single component, say $\alpha_{2,0;2,0} = \alpha_Q$,

$$\alpha_{2,m;2,m'} = \alpha_Q \delta_{mm'} \tag{5}$$

and

$$\alpha_Q = -2E_{2,0;2,0}^{(2)} = -2E^{(2)}. \tag{6}$$

The quantity α_Q is simply the atomic quadrupole polarizability defined by Dalgarno [4] and is equal to twice of the constant C introduced by Buckingham [1].

2.2. Survey of the EFV GTO concept for the field gradient perturbation

The EFV GTO's for the electric field gradient perturbation [18] have been defined by a reference to the exact solution of the corresponding perturbed spherical harmonic oscillator problem [22]. This approach is analogous to that utilized previously in the case of the EFV GTO bases for the dipole polarizability calculations [10, 14]. However, in the case of the field gradient perturbation the basis set modification is achieved through the field gradient dependence of the orbital exponents. For this reason it was necessary to generalize the concept of a single orbital exponent a_i to the second-rank tensor $\boldsymbol{a}_i$, whose cartesian components for the unperturbed system $a_{i,\mu\nu}(0)$ are given by [18]

$$a_{i,\mu\nu}(0) = a_i\delta_{\mu\nu}. \tag{7}$$

In order to define the pertinent EFV GTO's let us assume that a given unperturbed problem has already been solved using the initial GTO basis set $\{\chi_1(\boldsymbol{r}; \boldsymbol{a}_1(0)), \chi_2(\boldsymbol{r}; \boldsymbol{a}_2(0)), ..., \chi_m(\boldsymbol{r}; \boldsymbol{a}_m(0))\}$, where $\boldsymbol{r}$ is the electron position vector and the tensor exponents for the unperturbed problem are given by Eq. (7). For the sake of simplicity we shall also consider only a single component of the field gradient tensor, say $V_{2,0} = V$. Then, according to Part II of this series the resulting EFV GTO set will have the following form $\{\chi_1(\boldsymbol{r}; \boldsymbol{a}_1(V, \lambda)), \chi_2(\boldsymbol{r}; \boldsymbol{a}_2(V, \lambda)), ..., \chi_m(\boldsymbol{r}; \boldsymbol{a}_m(V, \lambda))\}$ with the field gradient dependent orbital exponent tensors given by

$$a_{i,xx}(V, \lambda) = a_{i,yy}(V, \lambda) = a_i\left[1 + \frac{\lambda V}{4a_i^2}\right]^{1/2}, \tag{8}$$

$$a_{i,zz}(V, \lambda) = a_i\left[1 - 2\frac{\lambda V}{4a_i^2}\right]^{1/2}, \tag{9}$$

and

$$a_{i,\mu\nu}(V, \lambda) = 0 \quad \text{for} \quad \mu \neq \nu. \tag{10}$$

The additional parameter λ was introduced in order to account for the difference between the corresponding solution of the perturbed harmonic oscillator problem and the modification of orbitals in a many-electron system [18]. The numerical value of this parameter is obtained variationally through the minimization of the second-order energy expression [18, 25]. The form of the EFV GTO's displayed in this section will help to introduce the corresponding EFV STO bases.

2.3. The EFV STO basis set for the field gradient perturbation

According to the material presented in Section 2.2 the exponential part of each primitive GTO, i.e. $\exp(-a_ir^2)$, in the presence of the quadrupole perturbation term (1) with $V_{2,m} = V_{m,0}$ will undergo the following distortion

$$\exp(-a_ir^2) \xrightarrow[-Q_{2,0}V]{} \exp(-a_{i,xx}x^2 - a_{i,yy}y^2 - a_{i,zz}z^2), \tag{11}$$

where the modified exponents are given by Eqs. (8) and (9) and determine the explicit dependence of each EFV GTO on the strength of the external perturbation. This is the

most important result, for it allows for a straightforward introduction of the relevant EFV STO functions.

It is known that the exponential part of each STO, i.e. $\exp(-\beta_i r)$, can be expressed in terms of the following integral transform [26]

$$\exp(-\beta_i r) = \frac{\beta_i}{2\sqrt{\pi}} \int_0^\infty s^{-3/2} \exp(-\beta_i^2/4s) \exp(-sr^2)ds. \tag{12}$$

Once the field gradient dependence of the exponential Gaussian term in the integrand of (12) is known one can generate the analytic perturbation dependence of the STO's by a simple substitution of the appropriate counterpart of Eq. (11). This procedure defines the EFV set corresponding to a given initial set of STO's. By virtue of Eqs. (8) and (9) the EFV STO's will explicitly depend on the perturbation strength V. They will also depend on the additional parameter λ which is to be determined during the second-order energy calculations.

If we denote by $\chi_i(r; \beta_i(0)) = \chi_i(0)$ the initial STO's for employed for the unperturbed system, then the EFV STO functions for the perturbed problem can be written as $\chi_i(r; \beta_i, \lambda, V) = \chi_i(\lambda, V)$. The explicit dependence on V follows from the integral transformation (12) and Eq. (11). The appropriate substitutions lead to the following power series expansion of $\chi_i(\lambda, V)$

$$\chi_i(\lambda, V) = \chi_i(0)\left\{1 + \tfrac{1}{2}Q_{2,0}(1+\beta_i r)\frac{1}{\beta_i^2}\lambda V + \left[\tfrac{1}{8}Q_{2,0}^2\left[1 + (1+\beta_i r) + (1+\beta_i r)^2\right]\frac{1}{\beta_i^4}\right.\right.$$

$$\left.\left. + \tfrac{1}{8}(Q_{2,0}+r^2)\left[5 + 6(1+\beta_i r) + 3(1+\beta_i r)^2 + (1+\beta_i r)^3\right]\frac{1}{\beta_i^6}\right]\lambda^2 V^2 + \dots\right\}, \tag{13}$$

where

$$Q_{2,0} = \tfrac{1}{2}(3z^2 - r^2). \tag{14}$$

Even if the initial STO is normalized this is not the case of $\chi_i(\lambda, V)$. Thus, although the expansion (13) is the same for any STO the resulting EFV STO's will have, in general, distinct normalization constants.

Some general features of the EFV STO's for the quadrupole perturbations are of particular interest. First of all, the EFV STO's exhibit a strong dependence on the orbital exponents. It follows from Eq. (13) that the smaller is the orbital exponent the larger will be the field gradient induced distortion of a given initial STO. This is precisely the feature we need to have a reasonable description of the system response to the external perturbation. For the electric field perturbations this is the outermost part of a given system which is expected to be primarily modified. This part in turn is usually described by orbitals with relatively small exponents. Secondly let us notice that both λ and V enter expansion (13) always as a product λV. This is the feature which allows one to show that the n-th order energy can be treated as the n-th order polynom in λ [14, 25, 27]. Finally, let us point out

that for a given initial STO set the corresponding EFV STO set has the same dimension and its dependence on V is assumed to take care of all the perturbation effects. The expansion (13) shows that using the EFV STO's is to some extent equivalent to the initial basis set augmentation with the higher STO's. These are implicitly generated within the present method.

3. Calculation of atomic quadrupole polarizabilities using EFV STO's

3.1. Hartree–Fock perturbation theory for non-orthogonal perturbation--dependent bases

The calculations reported in this paper have been carried out using the coupled Hartree–Fock (CHF) perturbation theory. However, due to both the non-orthogonality and the perturbation dependence of the EFV STO basis set, the standard CHF method [4–6, 28] which assumes that the basis functions are orthonormal and independent of the external perturbation must be replaced by its appropriate modified version [27]. A tremendous simplification of the general perturbation equations [27] follows from some specific symmetry properties of systems considered in this paper. These are the atomic He- and Be-like systems whose unperturbed orbitals are expressible solely in terms of the s-type STO's. In this particular case the second-order energy formula [27] can be simplified to

$$E^{(2)} = 2 \, \mathrm{Tr} \left[f^{(2)} - h^{(0)} R^{(0)} S^{(2)} + \tfrac{1}{2} \, G(R^{(0)}, g^{(2)}) \right] R^{(0)}, \qquad (15)$$

where $R^{(0)}$ is the zeroth-order density matrix in the unperturbed STO set and $h^{(0)}$ is the corresponding matrix of the unperturbed HF Hamiltonian. Similarly $f^{(2)}$ and $S^{(2)}$ collect the second-order terms of the f and the overlap matrix S, respectively. The f matrix involves the elements of the one-electron bare nuclei plus perturbation Hamiltonian. $g^{(2)}$ is the supermatrix of the second-order two-electron integrals and G is the matrix of two-electron terms of the HF operator. More detailed expressions for these matrices can be found in Refs. [14, 25, 27].

Due to the symmetry of both the unperturbed systems considered in this paper and the perturbation operator (1) the first-order perturbed density matrix $R^{(1)}$ does identically vanish. Furthermore, since the parameter λ enters all matrix elements as a product with V, the second-order energy is the parabolic function of λ [14, 27]. Thus, $E^{(2)} = E^{(2)}(\lambda)$ can be minimized with respect to λ and the resulting minimum will correspond to the best variational result within the EFV STO approximation [25].

The calculations reported in the subsequent sections of this paper have been carried out using a fully analytic computational scheme, i.e. all the perturbed matrices have been calculated analytically using the appropriate expansions and performing a direct analytic integration.

3.2. Quadrupole polarizability of the hydrogen atom

There are two interesting aspects of the EFV STO calculation for the hydrogen atom. First of all the $1s$ STO with $\beta_i = 1$ is the exact solution for the unperturbed problem. Secondly, the exact value of the quadrupole polarizability of H is known and amounts

to 15.0 a.u. [4]. Thus, the second-order energy calculated using the EFV STO approach will not depend on the accuracy of the unperturbed solution and can also be checked against the corresponding exact value. The present method leads to

$$\alpha_Q(\lambda) = -2E^{(2)}(\lambda) = 40.5\lambda - 27.3750\lambda^2 \tag{16}$$

and the second-order energy minimization results in the optimal value of λ, $\hat{\lambda} = 0.739726$. This corresponds to $\alpha_Q(\hat{\lambda}) = 14.979452$ a.u. which is almost the exact value and shows that the EFV STO approach may give the quadrupole polarizabilities of high accuracy.

Another test of the reliability of the EFV STO method is supplied by a direct comparison of the accurate and approximate first-order perturbed wave function $\Psi^{(1)}$. How-
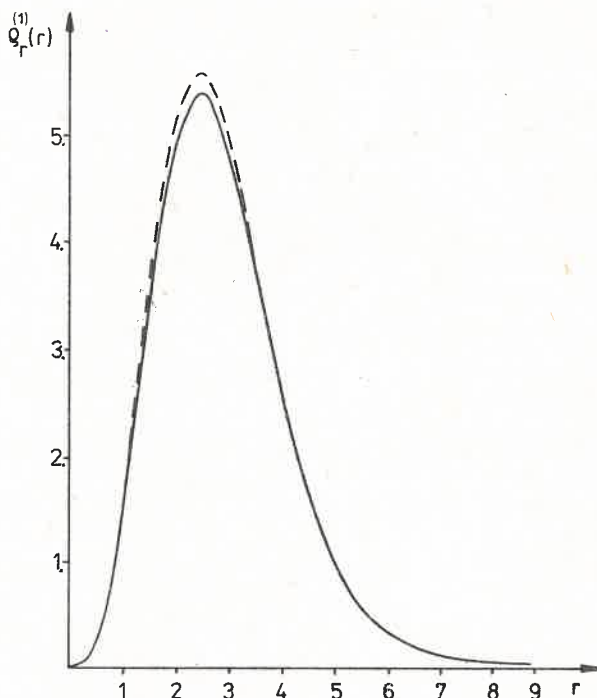

Fig. 1. Radial first-order density function ($\varrho_r^{(1)}$) for the hydrogen atom: — — — corresponds to the exact result and ——— represents the λ-optimized EFV STO function. Both $\varrho_r^{(1)}$ and the electron-nucleus distance r are given in atomic units

ever, since the second-order energy involves both the unperturbed ($\Psi^{(0)}$) and the perturbed function through the element $\langle \Psi^{(0)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle$ it appears to be more instructive to compare the pertinent first-order spinless one-electron densities [29]. Within the one-electron approximation these quantities are defined by

$$\varrho^{(1)}(\boldsymbol{r}; \lambda) = \sum_k n_k(\psi_k^{(0)}(\boldsymbol{r})\psi_k^{(1)*}(\boldsymbol{r}; \lambda) + \psi_k^{(0)*}(\boldsymbol{r})\psi_k^{(1)}(\boldsymbol{r}; \lambda)), \tag{17}$$

where $\psi_k^{(0)}$ and $\psi_k^{(1)}$ are the unperturbed and first-order perturbed orbitals, respectively, and n_k is the orbital occupation number. For the exact solutions $\psi_k^{(1)}(r, \lambda)$ becomes the pertinent exact first-order perturbed function and is obviously independent of λ. In the case of atomic systems and real orbitals it is enough to compare only the radial first-order densities. For the hydrogen atom such a comparison is presented in Fig. 1. As could have been expected from the α_Q result the difference between the exact and approximate (for $\hat{\lambda}$) first-order radial density is small. It becomes almost negligible for larger distances from the nucleus. This region is, on the other hand, of primary importance for the calculation of α_Q.

The results obtained for the hydrogen atom undoubtedly indicate that the EFV STO method is the right approach to the calculation of atomic quadrupole polarizabilities. However, for systems with more than one electron the α_Q value will also be influenced by the inaccuracy of the approximate unperturbed HF orbitals and this problem requires a rather detailed analysis.

3.3. EFV STO CHF calculations of the quadrupole polarizability for 2- and 4-electron atomic systems

Our previous EFV GTO calculations for H, He and Be [18] have shown that the convergence of α_Q for the GTO bases is quite slow. Since the number of STO's required in accurate atomic calculations is much smaller than the number of GTO's and since the STO bases provide usually a better description of the outer atomic regions the EFV STO approach could be even superior to that of Part II of this series [18]. Let us first focus our attention on the α_Q calculations for He and Be which can be directly compared with our previous EFV GTO results [18].

A variety of distinct STO bases of different accuracy has been employed in the calculations for He and Be. Their quality can be to some extent estimated from the unperturbed energy values $E^{(0)}$. These as well as the calculated second-order energies and the optimized values of λ are listed for both atoms in Table I. Among the initial STO bases utilized for He the best appears to be the optimized 5 STO set of Clementi [30]. For the beryllium atom there are two STO bases of presumably very high accuracy. One of them is the 5 STO set of Clementi which comprises two $1s$ and three $2s$ carefully optimized Slater-type functions. The other is the 12 STO set of Roothaan et al. [31] which involves higher, up to $4s$, STO's, though less selectively optimized. From the point of view of $E^{(0)}$ these two bases are practically equivalent. However, the resulting optimized $E^{(2)}$ values differ by almost 2 a.u.; a comparison with the reference CHF data which is carried out in Table II appears to indicate that the 12 EFV STO value is presumably the most reliable one.

Just as for the hydrogen atom the calculated radial parts of the first-order density functions for He and Be for some selected bases are shown in Fig. 2. Let us add that for He the 2 EFV STO function of Clementi [30] gives practically the same plot as the 2 EFV STO function following from the tables by Bagus et al. [32]. Almost the same quality of the density function is observed for the 4 STO and 5 STO sets of Bagus et al. [32] and the 5 STO set of Clementi [30]. All they give the density plots nearly coinciding with that for the 6 STO set of Clementi [30] and for this reason have not been explicitly shown in Fig. 2.

TABLE I

Initial STO basis set dependence of the optimized second-order energies due to field gradient perturbation for He and Be. The reported values of $E^{(2)}$ correspond to the optimized parameter λ

|	He				Be		
STO/EFV STO basis set dimension	$E^{(0)}$ (in a.u.)	Optimized λ	$E^{(2)}$ (in a.u.)	STO/EFV STO basis set dimension	$E^{(0)}$ (in a.u.)	Optimized λ	$E^{(2)}$ (in a.u.)
1	−2.847656	2.077	−1.821	2 [32]	−14.556740	1.107	−173.616
2 [32]	−2.8616727	0.736	−1.168	3 [32]	−14.572093	1.269	−179.655
2 [30]	−2.8616700	0.726	−1.165	4 [32]	−14.572988	0.920	−166.784
3 [32]	−2.8516796	0.628	−1.162	5 [30]	−14.573014	0.903	−166.428
4 [30]	−2.8616785	0.676	−1.128	5 [32]	−14.573021	0.930	−167.938
5 [30]	−2.8616799	0.707	−1.162	6 [30]	−14.573020	0.927	−167.826
				12 [31]	−14.573020	0.937	−169.781
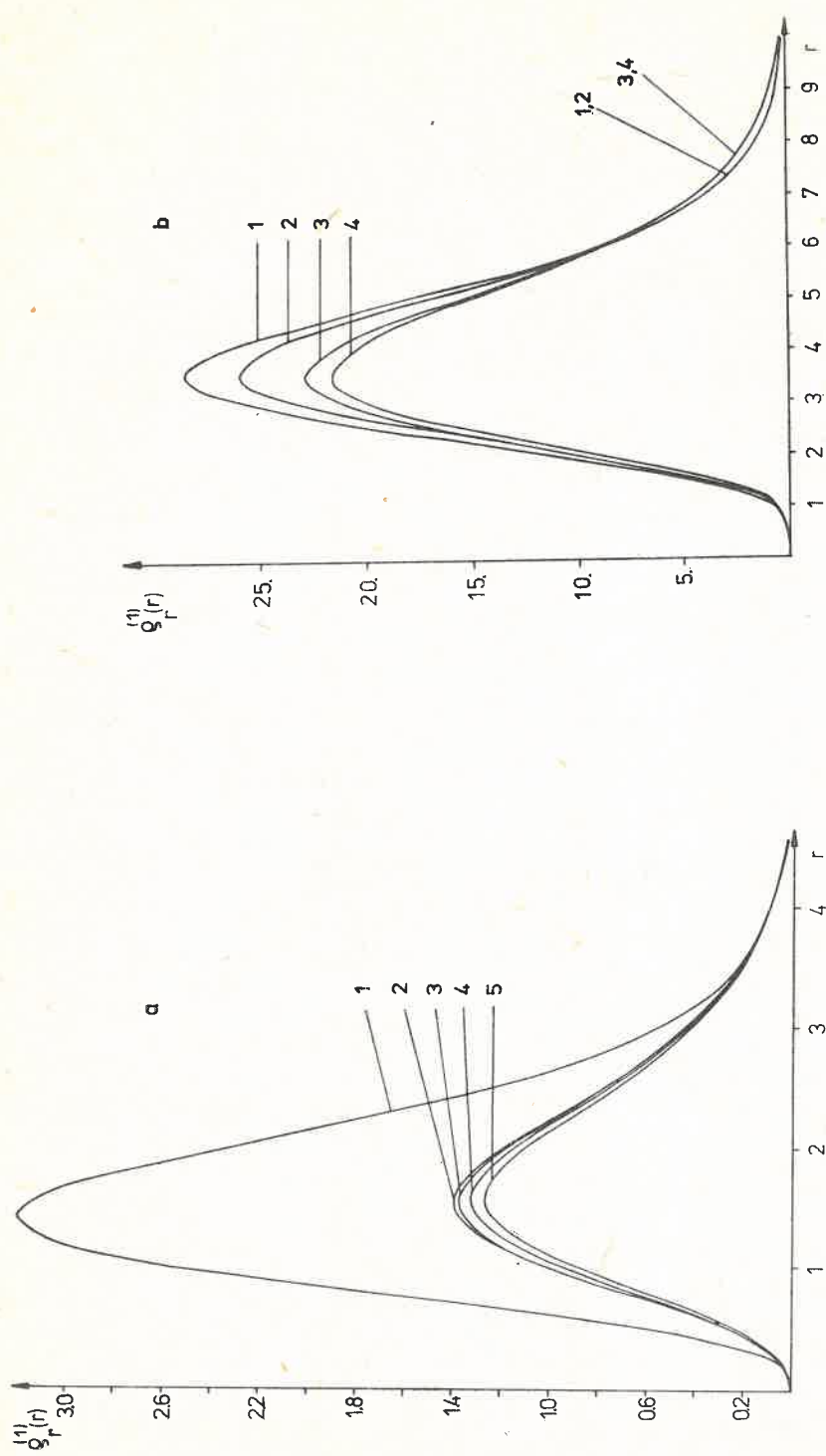
Fig. 2. Radial first-order density function ($\varrho_r^{(1)}$) vs the electron-nucleus distance r. All entries in a.u. a) He atom: 1 — 1 EFV STO basis set, 2 — EFV STO basis set, $3.$ — 2 EFV STO basis set, 4 — 5 EFV STO basis set, 5 — 4 EFV STO basis set (this is presumably the most accurate result). All STO bases taken from Ref. [30]. b) Be atom: 1 — 3 EFV STO basis set [32], 2 — 2 EFV STO basis set [32], 3 — 12 EFV STO basis set [31], 4 — 6 EFV STO basis set [30]. The curves marked as 3 and 4 correspond to the most accurate λ-optimized EFV STO results

TABLE II

A comparison of the EFV STO and other CHF results for the quadrupole polarizability of two- and four- -electron atomic systems. All entries in $Å^5$

Atom or ion	EFV STO CHF (this work) [a,b]	Reference CHF results		
		Ref. [33]	Ref. [34]	Other sources
He	0.0965	0.0965	0.0967	0.0964 [18][c], 0.0979 [35], 0.0965 [36]
Li$^+$	$0.4639 \cdot 10^{-2}$	$0.4653 \cdot 10^{-2}$	$0.4699 \cdot 10^{-2}$	
Be^{2+}	$0.6221 \cdot 10^{-3}$	$0.6347 \cdot 10^{-3}$	$0.6424 \cdot 10^{-3}$	
B^{3+}	$0.1403 \cdot 10^{-3}$	$0.1422 \cdot 10^{-3}$	$0.1435 \cdot 10^{-3}$	
C^{4+}	$0.4266 \cdot 10^{-4}$	$0.4299 \cdot 10^{-4}$	$0.4330 \cdot 10^{-4}$	
N^{5+}	$0.1577 \cdot 10^{-4}$	$0.1587 \cdot 10^{-4}$	$0.1596 \cdot 10^{-4}$	
O^{6+}	$0.6722 \cdot 10^{-5}$	$0.6754 \cdot 10^{-5}$		
F^{7+}	$0.3154 \cdot 10^{-5}$	$0.3198 \cdot 10^{-5}$		
Ne^{8+}	$0.1660 \cdot 10^{-5}$	$0.1645 \cdot 10^{-5}$		
Be	14.09		14.4	14.2 [37], 14.15 [18][c]
B$^+$	1.114		1.256	
C^{2+}	0.2071		0.2262	
N^{3+}	$0.5673 \cdot 10^{-1}$		$0.6135 \cdot 10^{-1}$	
O^{4+}	$0.1971 \cdot 10^{-1}$		$0.2127 \cdot 10^{-1}$	
F^{5+}	$0.8057 \cdot 10^{-2}$		$0.8693 \cdot 10^{-2}$	
Ne^{6+}	$0.3710 \cdot 10^{-2}$			

[a] Optimized EFV STO CHF results obtained with 5 STO set for He, 4 STO sets for all two-electron ions, 12 STO set for Be, and 5 STO sets for all four-electron ions. All the STO basis sets taken from Clementi's tables [30] except for the 12 STO set for Be [31].

[b] 1 a.u. of quadrupole polarizability $= 0.041496 \cdot 10^{-40}$ cm^5 $= 0.041496$ Å^5 $= 0.46170 \cdot 10^{-61}$ C^{2}m^{4}J^{-1}. Conversion factors calculated from the values of fundamental constants taken from Ref. [38].

[c] The EFV GTO CHF results of Part II [18].

It is rather surprising that the 1 STO set for He gives a very poor result for $E^{(2)}$, while the 2 STO (minimal) set for Be turns out to be quite reliable.

The final values of the calculated quadrupole polarizabilities for He and Be as well as our results for the corresponding isoelectronic ions are listed in Table II. They are compared with other CHF results obtained by using fixed and appropriately larger bases. For two-electron systems our EFV STO results computed using the 5 STO set for He and the 4 STO sets for ions [30] are practically as good as the recent highly accurate data reported by Stewart et al. [33]. Of note is, however, that for charged systems our results are more or less systematically lower than those of Stewart et al. [33] and Langhoff et al. [34], the latter being higher than the former ones.

With regard to the four-electron series, the present value for Be is rather close to the reference CHF results. However, once again for charged systems our data are systematically

smaller than those by Langhoff et al. [34]. The present EFV STO results are also compared with the He and Be polarizabilities calculated previously within the EFV GTO CHF approach [18].

4. Discussion and conclusions

The final results of the EFV STO CHF calculations reported in Table II indicate, first of all, that the present approach can provide quite accurate values of quadrupole polarizabilities of atomic systems. However, in order to achieve sufficiently high accuracy of the computed polarizabilities one has to use quite large initial STO bases. As indicated by our comparisons for cations, the accuracy of the EFV STO polarizabilities appears to be highly sensitive to the initial basis set quality. It is worth attention that the appropriate EFV STO bases generated for the dipole polarizability calculations have been found far more promising [14].

According to the data of Table II, the EFV STO bases seem to be, surprisingly enough, less efficient than the EFV GTO bases utilized in Part II [18]. It is important to notice that the basis set size dependence of the EFV STO results is not as uniform as that observed for the EFV GTO bases. This can be, however, due to incomplete optimization of the STO exponents, or at least due to slightly non-systematic build up of larger bases from the smaller ones.

Nonetheless, one has to conclude that the EFV STO CHF scheme requires quite accurate initial STO bases. This conclusion makes questionable any extension of this approach to molecules and one should hope that the performance of the EFV GTO CHF method will be in this case good enough. However, as far as the atomic systems are concerned the EFV STO CHF method is expected to be quite valuable, specifically for the calculation of quadrupole polarizabilities of different electronic states of open-shell systems. The appropriate CHF scheme is currently under consideration and the corresponding calculations will be reported in near future.

REFERENCES

[1] A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
[2] A. T. Amos, R. J. Crispin, in *Theoretical Chemistry. Advances and Perspectives,* Eds. H. Eyring, D. Henderson, Academic Press, New York 1976, vol. 2, p. 1.
[3] R. M. Glover, F. Weinhold, *J. Chem. Phys.* **65**, 4913 (1976).
[4] A. Dalgarno, *Adv. Phys.* **11**, 281 (1962).
[5] R. McWeeny, *Phys. Rev.* **126**, 1028 (1962).
[6] R. M. Stevens, R. M. Pitzer, W. N. Lipscomb, *J. Chem. Phys.* **38**, 550 (1963).
[7] H.-J. Werner, W. Meyer, *Phys. Rev.* **A13**, 13 (1976); H.-J. Werner, W. Meyer, *Mol. Phys.* **31**, 855 (1976).
[8] P. Swanstrøm, W. P. Kraemer, G. H. F. Diercksen, *Theor. Chim. Acta* **44**, 109 (1977).
[9] P. Lazzeretti, B. Cadioli, U. Pincelli, *Int. J. Quantum Chem.* **10**, 771 (1976).
[10] A. J. Sadlej, *Chem. Phys. Lett.* **47**, 50 (1977).

[11] V. P. Gutschick, V. McKoy, *J. Chem. Phys.* **58**, 2397 (1973).

[12] H.-J. Werner, W. Meyer, *Phys. Rev.* **A13**, 13 (1976).

[13] P. A. Christiansen, E. A. McCullough, Jr., *Chem. Phys. Lett.* **55**, 439 (1978).

[14] A. J. Sadlej, *Acta Phys. Pol.* **A53**, 297 (1978). (Part I)

[15] A. J. Sadlej, *Theor. Chim. Acta* **47**, 205 (1978).

[16] A. J. Sadlej, *Mol. Phys.* **34**, 731 (1977).

[17] A. J. Sadlej, *Mol. Phys.* **36**, 1701 (1978).

[18] K. Woliński, A. J. Sadlej, *Chem. Phys. Lett.* **64**, 51 (1979)

[19] L. Adamowicz, A. J. Sadlej, *Chem. Phys. Lett.* **53**, 377 (1978).

[20] K. Szalewicz, L. Adamowicz, A. J. Sadlej, *Chem. Phys. Lett.* **61**, 548 (1979).

[21] A. J. Sadlej, *J. Phys. Chem.* **83**, 1653 (1979).

[22] A. Messiah, *Quantum Mechanics,* North-Holland, Amsterdam 1961.

[23] J. L. Prather, *Atomic Energy Levels in Crystals,* NBS Monograph 19, NBS, Washington 1961.

[24] F. Mulder, M. C. van Hemert, P. E. S. Wormer, A. van der Avoird, *Theor. Chim. Acta* **46**, 39 (1977).

[25] S. T. Epstein, A. J. Sadlej, *Int. J. Quantum Chem.,* **15**, 147 (1979).

[26] I. Shavitt, M. Karplus, *J. Chem. Phys.* **43**, 415 (1965).

[27] J. L. Dodds, R. McWeeny, A. J. Sadlej, *Mol. Phys.* **34**, 1779 (1977).

[28] G. Diercksen, R. McWeeny, *J. Chem. Phys.* **44**, 3554 (1966).

[29] R. McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960).

[30] E. Clementi, *IBM J. Res. Dev.,* Suppl. **9**, 2 (1965).

[31] C. C. J. Roothaan, L. M. Sachs, A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

[32] P. S. Bagus, T. L. Gilbert, C. C. J. Roothaan, *J. Chem. Phys.* **56**, 5195 (1972); National Auxiliary Publication Service Document 01767.

[33] R. F. Stewart, B. C. Webster, *J. Chem. Soc., Faraday Trans.* II **69**, 1685 (1973).

[34] P. W. Langhoff, M. Karplus, R. P. Hurst, *J. Chem. Phys.* **44**, 505 (1966).

[35] A. Dalgarno, J. M. McNamee, *Proc. Phys. Soc.* **77**, 673 (1961).

[36] R. P. McEachran, A. G. Ryman, A. D. Stauffer, *J. Phys. B* **10**, L681 (1977).

[37] A. Dalgarno, H. A. J. McIntyre, *Proc. Phys. Soc.* **85**, 47 (1965).

[38] E. R. Cohen, B. N. Taylor, *J. Phys. Chem. Ref. Data* **2**, 663 (1973).