

# Relativistic Calculations of Static Electric Polarizabilities for Alkaline-Earth-Metals and their Isoelectronic Sequences

Radosław Szmytkowski

Institute of Theoretical Physics and Astrophysics, University of Gdańsk, Wita Stwosza 57, 80-952 Gdańsk, Poland

and

Abu Mohamed Alhasan

Physics Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt

Received November 23, 1994; accepted in revised form February 20, 1995

## Abstract

Dipole and quadrupole static electric polarizabilities of alkaline-earth-metals (Be, Mg, Ca, Sr, Ba, and Ra) and closed-shell members of their isoelectronic sequences ( $B^+$  to  $Rf^{100+}$ ,  $Al^+$  to  $Rf^{92+}$ ,  $Y^+$ , and  $Ac^+$ ) were calculated in the relativistic polarized orbital approximation which is the most elaborate approximation within the restricted Dirac–Hartree–Fock framework. For atoms our results are 15–25% higher than those of more elaborate multi-configurational calculations primarily due to neglect of  $np^2$  configurations in the description of the ground-state wave functions but for ions the present data are expected to be more accurate.

## 1. Introduction

Static electric polarizabilities of atoms and ions are among their most important properties and this explains a continuous effort in determining their accurate values both experimentally and theoretically [1–4]. Among many theoretical approaches one of the most fruitful was the polarized orbital approximation based on the coupled Hartree–Fock equations (see, for example, Refs [5, 6]). This method was successfully applied for calculations of the first four multipole polarizabilities for closed-shell atoms and low-charged ions with valence configurations  $ns^2$  [7],  $ns^2np^6$  [8, 9] and  $nd^{10}$  [10]. Although these calculations were carried out very carefully, the results obtained for heavier atoms and ions were not quite reliable since the relativistic effects were not taken into account. The relativistic generalization of the polarized orbital method, based on the coupled Dirac–Hartree–Fock equations, was given by Kolb *et al.* [11] (see also Ref. [13]) and applied to calculations of dipole and quadrupole polarizabilities for  $ns^2np^6$  and  $nd^{10}$  isoelectronic sequences [12]. Results completely confirmed necessity of using the relativistic approach.

In the present paper we extend the relativistic calculations of Kolb *et al.* [11, 12] to alkaline-earth-metals (Be, Mg, Ca, Sr, Ba, and Ra) and closed-shell members of their isoelectronic sequences ( $B^+$  to  $Rf^{100+}$ ,  $Al^+$  to  $Rf^{92+}$ ,  $Y^+$ , and  $Ac^+$ ). For majority of discussed ions, especially for those with large net charges, our data are probably the only available.

## 2. Method

We consider an  $N$ -electron closed-shell target (atom or ion) with an infinitely heavy point nucleus of charge  $+Ze$  put

at the origin of the coordinate system. We assume that in absence of any external field its electronic cloud in the ground state is characterized by a wave function  $\Phi^{(0)}(\mathbf{R})$ , where  $\mathbf{R}$  stands for all target electrons spatial coordinates.

We place the target in a static electric field produced by a distant point charge  $+e$  situated at a point characterized by a position vector  $\mathbf{x}$ , with  $x \gg a_0$ , where  $a_0$  is the Bohr radius. Static electric  $2^k$ -pole polarizabilities  $\alpha_k$  ( $k = 1, 2, \dots$ ) of the target are defined as coefficients in an asymptotic expansion of the second-order perturbation theory correction to the target-charge interaction energy [1]

$$\langle \Phi^{(0)}(\mathbf{R}) | V(\mathbf{R}, \mathbf{x}) | \Phi^{(1)}(\mathbf{R}, \mathbf{x}) \rangle_{\mathbf{R}} \xrightarrow{x \rightarrow \infty} \sum_{k=1}^{\infty} \frac{-\alpha_k e^2}{2x^{2k+2}}, \quad (1)$$

where

$$V(\mathbf{R}, \mathbf{x}) = - \sum_{i=1}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{x}|} \quad (2)$$

is an operator describing a Coulomb interaction between the perturbing charge and target electrons,  $\mathbf{r}_i$  denotes a position vector of the  $i$ th target electron, and  $\Phi^{(1)}(\mathbf{R}, \mathbf{x})$  is the first-order correction to the wave function  $\Phi^{(0)}(\mathbf{R})$  due to the perturbation  $V$ . In the relativistic polarized orbital approximation one assumes that the ground state of the isolated target may be described by a determinant

$$\Phi^{(0)}(\mathbf{R}) = (N!)^{-1/2} \det |\phi_1^{(0)}, \phi_2^{(0)}, \dots, \phi_N^{(0)}| \quad (3)$$

built of orthonormalized one-electron four-component orbitals  $\phi_i^{(0)}(\mathbf{r})$  satisfying the Dirac–Hartree–Fock (DHF) equations

$$\left[ h + \sum_{j=1}^N \left( \left\langle \phi_j^{(0)} \left| \frac{e^2}{r_{12}} \right| \phi_j^{(0)} \right\rangle_2 - |\phi_j^{(0)}\rangle \frac{e^2}{r_{12}} \langle \phi_j^{(0)} |_2 \right) \right] |\phi_i^{(0)}\rangle - \sum_{j=1}^N E_{ji}^{(0)} |\phi_j^{(0)}\rangle = 0. \quad (4)$$

Here  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  and

$$h(\mathbf{r}) = -i\hbar c \boldsymbol{\alpha} \cdot \nabla + \beta m c^2 - \frac{Z e^2}{r}, \quad (5)$$

where the matrices  $\boldsymbol{\alpha}$  (not to be confused with  $\alpha_k$ ) and  $\beta$  are defined in terms of a unit  $2 \times 2$  matrix  $I_2$  and the Pauli matrices  $\boldsymbol{\sigma}$  in a following way [14]

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}. \quad (6)$$

The first-order correction  $\Phi^{(1)}(\mathbf{R}, \mathbf{x})$  to the wave function  $\Phi^{(0)}(\mathbf{R})$ , which enters eq. (1), has a form

$$\Phi^{(1)}(\mathbf{R}, \mathbf{x}) = (N!)^{-1/2} \sum_{i=1}^N \det |\phi_1^{(0)}, \phi_2^{(0)}, \dots, \phi_i^{(1)}, \dots, \phi_N^{(0)}|, \quad (7)$$

where the one-electron four-component corrections  $\phi_i^{(1)}(\mathbf{r}, \mathbf{x})$  to unperturbed orbitals  $\phi_i^{(0)}(\mathbf{r})$  satisfy the coupled Dirac–Hartree–Fock (CDHF) equations [11, 13]

$$\begin{aligned} & \left[ h + \sum_{j=1}^N \left( \left\langle \phi_j^{(0)} \left| \frac{e^2}{r_{12}} \right| \phi_j^{(0)} \right\rangle - |\phi_j^{(0)}\rangle \frac{e^2}{r_{12}} \langle \phi_j^{(0)}|_2 \right) \right] |\phi_i^{(1)}\rangle \\ & - \sum_{j=1}^N E_{ji}^{(0)} |\phi_j^{(1)}\rangle \\ & = -\mathcal{V} |\phi_i^{(0)}\rangle - \sum_{j=1}^N \left( \left\langle \phi_j^{(1)} \left| \frac{e^2}{r_{12}} \right| \phi_j^{(0)} \right\rangle_2 \right. \\ & \left. - |\phi_j^{(0)}\rangle \frac{e^2}{r_{12}} \langle \phi_j^{(1)}|_2 \right) |\phi_i^{(0)}\rangle \\ & - \sum_{j=1}^N \left( \left\langle \phi_j^{(0)} \left| \frac{e^2}{r_{12}} \right| \phi_j^{(1)} \right\rangle_2 - |\phi_j^{(1)}\rangle \frac{e^2}{r_{12}} \langle \phi_j^{(0)}|_2 \right) |\phi_i^{(0)}\rangle \\ & + \sum_{j=1}^N E_{ji}^{(1)} |\phi_j^{(0)}\rangle \end{aligned} \quad (8)$$

and are orthogonal to unperturbed orbitals:

$$\langle \phi_i^{(0)}(\mathbf{r}) | \phi_j^{(1)}(\mathbf{r}, \mathbf{x}) \rangle_{\mathbf{r}} = 0. \quad (9)$$

In eq. (8)

$$\mathcal{V}(\mathbf{r}, \mathbf{x}) = -\frac{e^2}{|\mathbf{r} - \mathbf{x}|}. \quad (10)$$

For the determinantal functions (3) and (7) the matrix element in eq. (1) may be simplified and one gets

$$\sum_{i=1}^N \langle \phi_i^{(0)}(\mathbf{r}) | \mathcal{V}(\mathbf{r}, \mathbf{x}) | \phi_i^{(1)}(\mathbf{r}, \mathbf{x}) \rangle_{\mathbf{r}} \xrightarrow{x \rightarrow \infty} \sum_{k=1}^{\infty} \frac{-\alpha_k e^2}{2x^{2k+2}}. \quad (11)$$

The CDHF equations (8) may be further reduced to a radial form and then solved numerically. Mathematical and computational details have been presented elsewhere [13, 15] and will not be repeated here.

The unperturbed atomic orbitals  $\phi_i^{(0)}$  were generated by the MCDHF code of Grant *et al.* [16] while the CDHF equations (8) yielding  $\phi_i^{(1)}$  were solved by the program POLAR [17]. As a test of correctness and accuracy of our computer code we calculated static dipole polarizabilities for closed-shell atoms belonging to the IIa, IIb, and 0 groups of the periodic system, both in the relativistic and nonrelativistic cases (in the latter case the speed of light  $c$  was simply multiplied by 1000). In both cases all atomic orbitals were allowed to be distorted. We found excellent agreement with results of similar relativistic calculations of Kolb and coworkers [11, 12] and nonrelativistic calculations of McEachran, Stauffer and their collaborators [7–9].

### 3. Results

#### 3.1. The beryllium isoelectronic sequence

Many theoretical calculations were performed for the dipole  $\alpha_1$  and quadrupole  $\alpha_2$  polarizabilities of beryllium atom (see, for example, Ref. [18] and references therein). Our values  $\alpha_1 = 45.59a_0^3$  and  $\alpha_2 = 342.1a_0^5$  are to be compared with

very accurate values  $\alpha_1 = 37.29a_0^3$  obtained by Muller *et al.* [19] and  $\alpha_2 = 295.7a_0^5$  calculated by Maroulis and Thakkar [18]. The observed discrepancy must be attributed to neglect of electron correlation effects in our description of the ground state of Be atoms, primarily the  $2p^2$  configuration.

Our results for the beryllium isoelectronic sequence are presented in Table I. For ions with  $Z \leq 15$  we agree well with similar nonrelativistic results of Markiewicz *et al.* [7], Lahiri and Mukherji [20] and Dalgarno and McIntyre [21]. For heavier ions for which relativity begins to play a signifi-

Table I. Dipole ( $\alpha_1$ ) and quadrupole ( $\alpha_2$ ) polarizabilities for the beryllium isoelectronic sequence. The number in brackets following the entries is the power of 10 by which the entry must be multiplied

Ion	$\alpha_1(a_0^3)$	$\alpha_2(a_0^5)$	Ion	$\alpha_1(a_0^3)$	$\alpha_2(a_0^5)$
Be	4.559 (+1)	3.421 (+2)	Xe <sup>50+</sup>	9.361 (−4)	1.182 (−6)
B <sup>+</sup>	1.137 (+1)	2.823 (+1)	Cs <sup>51+</sup>	8.657 (−4)	1.044 (−6)
C <sup>2+</sup>	4.499 (+0)	5.211 (+0)	Ba <sup>52+</sup>	8.015 (−4)	9.230 (−7)
N <sup>3+</sup>	2.230 (+0)	1.428 (+0)	La <sup>53+</sup>	7.428 (−4)	8.176 (−7)
O <sup>4+</sup>	1.265 (+0)	4.971 (−1)	Ce <sup>54+</sup>	6.891 (−4)	7.255 (−7)
F <sup>5+</sup>	7.853 (−1)	2.036 (−1)	Pr <sup>55+</sup>	6.399 (−4)	6.449 (−7)
Ne <sup>6+</sup>	5.203 (−1)	9.387 (−2)	Nd <sup>56+</sup>	5.947 (−4)	5.740 (−7)
Na <sup>7+</sup>	3.620 (−1)	4.733 (−2)	Pm <sup>57+</sup>	5.532 (−4)	5.117 (−7)
Mg <sup>8+</sup>	2.617 (−1)	2.562 (−2)	Sm <sup>58+</sup>	5.150 (−4)	4.568 (−7)
Al <sup>9+</sup>	1.950 (−1)	1.468 (−2)	Eu <sup>59+</sup>	4.798 (−4)	4.083 (−7)
Si <sup>10+</sup>	1.490 (−1)	8.819 (−3)	Gd <sup>60+</sup>	4.473 (−4)	3.655 (−7)
P <sup>11+</sup>	1.163 (−1)	5.513 (−3)	Tb <sup>61+</sup>	4.174 (−4)	3.275 (−7)
S <sup>12+</sup>	9.233 (−2)	3.565 (−3)	Dy <sup>62+</sup>	3.897 (−4)	2.939 (−7)
Cl <sup>13+</sup>	7.442 (−2)	2.374 (−3)	Ho <sup>63+</sup>	3.641 (−4)	2.640 (−7)
Ar <sup>14+</sup>	6.076 (−2)	1.621 (−3)	Er <sup>64+</sup>	3.403 (−4)	2.374 (−7)
K <sup>15+</sup>	5.017 (−2)	1.132 (−3)	Tm <sup>65+</sup>	3.183 (−4)	2.136 (−7)
Ca <sup>16+</sup>	4.183 (−2)	8.064 (−4)	Yb <sup>66+</sup>	2.979 (−4)	1.925 (−7)
Sc <sup>17+</sup>	3.518 (−2)	5.847 (−4)	Lu <sup>67+</sup>	2.789 (−4)	1.736 (−7)
Ti <sup>18+</sup>	2.982 (−2)	4.307 (−4)	Hf <sup>68+</sup>	2.613 (−4)	1.567 (−7)
V <sup>19+</sup>	2.545 (−2)	3.218 (−4)	Ta <sup>69+</sup>	2.449 (−4)	1.416 (−7)
Cr <sup>20+</sup>	2.185 (−2)	2.436 (−4)	W <sup>70+</sup>	2.296 (−4)	1.280 (−7)
Mn <sup>21+</sup>	1.887 (−2)	1.866 (−4)	Re <sup>71+</sup>	2.153 (−4)	1.158 (−7)
Fe <sup>22+</sup>	1.637 (−2)	1.445 (−4)	Os <sup>72+</sup>	2.020 (−4)	1.049 (−7)
Co <sup>23+</sup>	1.427 (−2)	1.130 (−4)	Ir <sup>73+</sup>	1.896 (−4)	9.504 (−8)
Ni <sup>24+</sup>	1.249 (−2)	8.916 (−5)	Pt <sup>74+</sup>	1.780 (−4)	8.618 (−8)
Cu <sup>25+</sup>	1.098 (−2)	7.095 (−5)	Au <sup>75+</sup>	1.672 (−4)	7.819 (−8)
Zn <sup>26+</sup>	9.684 (−3)	5.691 (−5)	Hg <sup>76+</sup>	1.570 (−4)	7.098 (−8)
Ga <sup>27+</sup>	8.569 (−3)	4.598 (−5)	Tl <sup>77+</sup>	1.475 (−4)	6.447 (−8)
Ge <sup>28+</sup>	7.606 (−3)	3.739 (−5)	Pb <sup>78+</sup>	1.386 (−4)	5.860 (−8)
As <sup>29+</sup>	6.770 (−3)	3.061 (−5)	Bi <sup>79+</sup>	1.303 (−4)	5.328 (−8)
Se <sup>30+</sup>	6.043 (−3)	2.520 (−5)	Po <sup>80+</sup>	1.224 (−4)	4.846 (−8)
Br <sup>31+</sup>	5.408 (−3)	2.086 (−5)	At <sup>81+</sup>	1.151 (−4)	4.410 (−8)
Kr <sup>32+</sup>	4.851 (−3)	1.736 (−5)	Rn <sup>82+</sup>	1.082 (−4)	4.015 (−8)
Rb <sup>33+</sup>	4.361 (−3)	1.452 (−5)	Fr <sup>83+</sup>	1.017 (−4)	3.656 (−8)
Sr <sup>34+</sup>	3.930 (−3)	1.219 (−5)	Ra <sup>84+</sup>	9.561 (−5)	3.331 (−8)
Y <sup>35+</sup>	3.548 (−3)	1.029 (−5)	Ac <sup>85+</sup>	8.988 (−5)	3.035 (−8)
Zr <sup>36+</sup>	3.210 (−3)	8.713 (−6)	Th <sup>86+</sup>	8.448 (−5)	2.766 (−8)
Nb <sup>37+</sup>	2.909 (−3)	7.409 (−6)	Pa <sup>87+</sup>	7.940 (−5)	2.522 (−8)
Mo <sup>38+</sup>	2.642 (−3)	6.323 (−6)	U <sup>88+</sup>	7.462 (−5)	2.299 (−8)
Tc <sup>39+</sup>	2.403 (−3)	5.415 (−6)	Np <sup>89+</sup>	7.012 (−5)	2.097 (−8)
Ru <sup>40+</sup>	2.190 (−3)	4.652 (−6)	Pu <sup>90+</sup>	6.588 (−5)	1.912 (−8)
Rh <sup>41+</sup>	1.999 (−3)	4.010 (−6)	Am <sup>91+</sup>	6.188 (−5)	1.744 (−8)
Pd <sup>42+</sup>	1.827 (−3)	3.466 (−6)	Cm <sup>92+</sup>	5.810 (−5)	1.591 (−8)
Ag <sup>43+</sup>	1.673 (−3)	3.004 (−6)	Bk <sup>93+</sup>	5.455 (−5)	1.451 (−8)
Cd <sup>44+</sup>	1.533 (−3)	2.611 (−6)	Cf <sup>94+</sup>	5.119 (−5)	1.323 (−8)
In <sup>45+</sup>	1.408 (−3)	2.275 (−6)	Es <sup>95+</sup>	4.802 (−5)	1.207 (−8)
Sn <sup>46+</sup>	1.294 (−3)	1.987 (−6)	Fm <sup>96+</sup>	4.503 (−5)	1.100 (−8)
Sb <sup>47+</sup>	1.191 (−3)	1.740 (−6)	Md <sup>97+</sup>	4.221 (−5)	1.003 (−8)
Te <sup>48+</sup>	1.098 (−3)	1.526 (−6)	No <sup>98+</sup>	3.954 (−5)	9.145 (−9)
I <sup>49+</sup>	1.013 (−3)	1.342 (−6)	Lr <sup>99+</sup>	3.703 (−5)	8.334 (−9)
			Rr <sup>100+</sup>	3.465 (−5)	7.592 (−9)

Table II. Dipole ( $\alpha_1$ ) and quadrupole ( $\alpha_2$ ) polarizabilities for the magnesium isoelectronic sequence. The number in brackets following the entries is the power of 10 by which the entry is to be multiplied

Ion	$\alpha_1(a_0^3)$	$\alpha_2(a_0^5)$	Ion	$\alpha_1(a_0^3)$	$\alpha_2(a_0^5)$
Mg	8.116 (+1)	9.216 (+2)	Ce <sup>46+</sup>	1.002 (-2)	2.133 (-4)
Al <sup>+</sup>	2.625 (+1)	1.291 (+2)	Pr <sup>47+</sup>	9.270 (-3)	1.882 (-4)
Si <sup>2+</sup>	1.248 (+1)	3.565 (+1)	Nd <sup>48+</sup>	8.585 (-3)	1.664 (-4)
P <sup>3+</sup>	7.082 (+0)	1.341 (+1)	Pm <sup>49+</sup>	7.959 (-3)	1.472 (-4)
S <sup>4+</sup>	4.459 (+0)	6.041 (+0)	Sm <sup>50+</sup>	7.385 (-3)	1.305 (-4)
Cl <sup>5-</sup>	3.008 (+0)	3.065 (+0)	Eu <sup>51+</sup>	6.858 (-3)	1.158 (-4)
Ar <sup>6+</sup>	2.132 (+0)	1.694 (+0)	Gd <sup>52+</sup>	6.375 (-3)	1.029 (-4)
K <sup>7+</sup>	1.569 (+0)	9.990 (-1)	Tb <sup>53+</sup>	5.930 (-3)	9.158 (-5)
Ca <sup>8+</sup>	1.189 (+0)	6.199 (-1)	Dy <sup>54+</sup>	5.521 (-3)	8.158 (-5)
Sc <sup>9+</sup>	9.233 (-1)	4.009 (-1)	Ho <sup>55+</sup>	5.145 (-3)	7.275 (-5)
Ti <sup>10+</sup>	7.309 (-1)	2.683 (-1)	Er <sup>56+</sup>	4.797 (-3)	6.495 (-5)
V <sup>11+</sup>	5.883 (-1)	1.848 (-1)	Tm <sup>57+</sup>	4.476 (-3)	5.804 (-5)
Cr <sup>12+</sup>	4.803 (-1)	1.305 (-1)	Yb <sup>58+</sup>	4.180 (-3)	5.193 (-5)
Mn <sup>13+</sup>	3.969 (-1)	9.411 (-2)	Lu <sup>59+</sup>	3.906 (-3)	4.650 (-5)
Fe <sup>14+</sup>	3.314 (-1)	6.917 (-2)	Hf <sup>60+</sup>	3.652 (-3)	4.167 (-5)
Co <sup>15-</sup>	2.794 (-1)	5.168 (-2)	Ta <sup>61+</sup>	3.417 (-3)	3.738 (-5)
Ni <sup>16+</sup>	2.375 (-1)	3.919 (-2)	W <sup>62+</sup>	3.199 (-3)	3.356 (-5)
Cu <sup>17+</sup>	2.033 (-1)	3.011 (-2)	Re <sup>63+</sup>	2.996 (-3)	3.016 (-5)
Zn <sup>18+</sup>	1.752 (-1)	2.340 (-2)	Os <sup>64+</sup>	2.808 (-3)	2.712 (-5)
Ga <sup>19+</sup>	1.519 (-1)	1.839 (-2)	Ir <sup>65+</sup>	2.634 (-3)	2.441 (-5)
Ge <sup>20+</sup>	1.324 (-1)	1.459 (-2)	Pt <sup>66+</sup>	2.471 (-3)	2.198 (-5)
As <sup>21+</sup>	1.160 (-1)	1.168 (-2)	Au <sup>67+</sup>	2.319 (-3)	1.981 (-5)
Se <sup>22+</sup>	1.020 (-1)	9.420 (-3)	Hg <sup>68+</sup>	2.178 (-3)	1.786 (-5)
Br <sup>23+</sup>	9.012 (-2)	7.657 (-3)	Tl <sup>69+</sup>	2.046 (-3)	1.612 (-5)
Kr <sup>24+</sup>	7.990 (-2)	6.266 (-3)	Pb <sup>70+</sup>	1.923 (-3)	1.455 (-5)
Rb <sup>25+</sup>	7.108 (-2)	5.160 (-3)	Bi <sup>71+</sup>	1.809 (-3)	1.315 (-5)
Sr <sup>26+</sup>	6.344 (-2)	4.274 (-3)	Po <sup>72+</sup>	1.701 (-3)	1.188 (-5)
Y <sup>27+</sup>	5.678 (-2)	3.559 (-3)	At <sup>73+</sup>	1.601 (-3)	1.075 (-5)
Zr <sup>28+</sup>	5.096 (-2)	2.978 (-3)	Rn <sup>74+</sup>	1.507 (-3)	9.724 (-6)
Nb <sup>29+</sup>	4.586 (-2)	2.504 (-3)	Fr <sup>75+</sup>	1.419 (-3)	8.803 (-6)
Mo <sup>30+</sup>	4.136 (-2)	2.114 (-3)	Ra <sup>76+</sup>	1.336 (-3)	7.972 (-6)
Tc <sup>31+</sup>	3.739 (-2)	1.793 (-3)	Ac <sup>77+</sup>	1.259 (-3)	7.223 (-6)
Ru <sup>32+</sup>	3.387 (-2)	1.526 (-3)	Th <sup>78+</sup>	1.186 (-3)	6.546 (-6)
Rh <sup>33+</sup>	3.074 (-2)	1.303 (-3)	Pa <sup>79+</sup>	1.118 (-3)	5.936 (-6)
Pd <sup>34+</sup>	2.795 (-2)	1.116 (-3)	U <sup>80+</sup>	1.054 (-3)	5.384 (-6)
Ag <sup>35+</sup>	2.546 (-2)	9.595 (-4)	Np <sup>81+</sup>	9.938 (-4)	4.884 (-6)
Cd <sup>36+</sup>	2.323 (-2)	8.272 (-4)	Pu <sup>82+</sup>	9.371 (-4)	4.433 (-6)
In <sup>37+</sup>	2.123 (-2)	7.150 (-4)	Am <sup>83+</sup>	8.838 (-4)	4.024 (-6)
Sn <sup>38+</sup>	1.943 (-2)	6.197 (-4)	Cm <sup>84+</sup>	8.335 (-4)	3.653 (-6)
Sb <sup>39+</sup>	1.781 (-2)	5.384 (-4)	Bk <sup>85+</sup>	7.862 (-4)	3.318 (-6)
Te <sup>40+</sup>	1.634 (-2)	4.689 (-4)	Cf <sup>86+</sup>	7.416 (-4)	3.013 (-6)
I <sup>41+</sup>	1.502 (-2)	4.092 (-4)	Es <sup>87+</sup>	6.995 (-4)	2.737 (-6)
Xe <sup>42+</sup>	1.382 (-2)	3.579 (-4)	Fm <sup>88+</sup>	6.597 (-4)	2.487 (-6)
Cs <sup>43+</sup>	1.273 (-2)	3.136 (-4)	Md <sup>89+</sup>	6.222 (-4)	2.259 (-6)
Ba <sup>44+</sup>	1.174 (-2)	2.753 (-4)	No <sup>90+</sup>	5.868 (-4)	2.053 (-6)
La <sup>45+</sup>	1.084 (-2)	2.421 (-4)	Lr <sup>91+</sup>	5.533 (-4)	1.865 (-6)
			Rf <sup>92+</sup>	5.216 (-4)	1.694 (-6)

cant role our results become lower than the corresponding nonrelativistic data. For instance, for Mo<sup>38+</sup> which is the heaviest ion in this sequence considered by Markiewicz *et al.* [7] the nonrelativistic dipole polarizability 4.028

Table III. Dipole ( $\alpha_1$ ) and quadrupole ( $\alpha_2$ ) polarizabilities for calcium, strontium, barium, radium, and two closed-shell ions. The number in brackets following the entries is the power of 10 by which the entry is to be multiplied

Atom	$\alpha_1(a_0^3)$	$\alpha_2(a_0^5)$	Ion	$\alpha_1(a_0^3)$	$\alpha_2(a_0^5)$
Ca	1.828 (+2)	3.526 (+3)			
Sr	2.326 (+2)	5.421 (+3)	Y <sup>+</sup>	9.040 (+1)	1.957 (+3)
Ba	3.240 (+2)	9.971 (+3)			
Ra	2.962 (+2)	8.940 (+3)	Ac <sup>+</sup>	1.229 (+2)	3.090 (+3)

$\times 10^{-3}a_0^3$  is about 35% higher than our relativistic result  $2.642 \times 10^{-3}a_0^3$ . Qualitatively this is understandable since generally relativistic ions are more compact than their non-relativistic counterparts and therefore less susceptible to influence of an external electric field.

### 3.2. The magnesium isoelectronic sequence

There have been a large number of calculations of the dipole polarizabilities for magnesium atom (see, for example, Ref. [22] and references therein). Among them the most accurate value seems to be  $\alpha_1 = 71.32a_0^3$  calculated by Reinsch and Meyer [23] (to be compared with our value  $81.16a_0^3$ ). For further comparison the reader is referred to the paper of Ray and Mukherjee [22] which includes a comprehensive list of values obtained by other authors. Again, our result overestimates more accurate data primarily due to neglect of the  $3p^2$  configuration in description of the ground-state wave function.

Our results for the magnesium isoelectronic sequence are presented in Table II. Again, for ions with low nuclear charge our results for  $\alpha_1$  agree quite well with the results of similar nonrelativistic calculations of Markiewicz *et al.* [7], Ray and Mukherjee [22], Bhattacharya *et al.* [24] and Stewart [25]. However, as could be expected, for heavier ions the discrepancy between the relativistic and nonrelativistic results increases reaching 10% for Mo<sup>30+</sup>, which is the heaviest ion in this sequence considered by Markiewicz *et al.* [7]. For  $\alpha_2$  we agree with the results obtained by the latter authors but agreement with results of calculations of Ray and Mukherjee [22] is not as satisfactory as for  $\alpha_1$ .

### 3.3. Calcium, strontium, barium and radium

For calcium, strontium, barium, and radium we have carried out our calculations only for one or two first members of their isoelectronic sequences since further along the sequences the ground states change character from closed-shell to open-shell [26]. The results are given in Table III. For Ca, Sr, and Ba our dipole polarizabilities ( $182.8a_0^3$ ,  $232.6a_0^3$ , and  $324.0a_0^3$ , respectively) can be compared with results of relativistic many-body-perturbation-theory calculations of Sadlej *et al.* [27] who obtained values  $152.0a_0^3$ ,  $194.0a_0^3$ , and  $277.1a_0^3$ , respectively. To the best of our knowledge no other data exist for Y<sup>+</sup> and Ac<sup>+</sup>.

Difference between present results and those of Sadlej *et al.* is again due to our neglect of correlation effects within the Dirac-Hartree-Fock approximation. Sadlej *et al.* showed that main correlation contributions to dipole polarizabilities came from  $3s^23p^64s^2$ ,  $4s^24p^65s^2$ , and  $4d^{10}5s^25p^66s^2$  subshells for Ca, Sr, and Ba, respectively. Consequently, the discrepancies are primarily due to our neglect of virtual electron excitations from these subshells.

## 4. Conclusions

We have performed relativistic *ab initio* calculations of static dipole and quadrupole polarizabilities for alkaline-earth-metals and closed-shell members of their isoelectronic sequences. The employed approach has been the relativistic polarized orbital approximation based on the coupled Dirac-Hartree-Fock equations which is the most elaborate approximation within the restricted Dirac-Hartree-Fock framework. It has been shown that inclusion of relativistic

effects leads to decrease in values of polarizabilities as compared with corresponding nonrelativistic results. It is understandable since generally relativistic atoms and ions are more compact than their nonrelativistic counterparts.

Comparison with other elaborate calculations performed for atoms shows that for alkaline-earth-metals our results are in error by about 15–25%. This is primarily due to neglect of  $np^2$  configurations in description of the ground-state wave functions. For ions our results are expected to be more accurate since further along the isoelectronic sequences energy differences between configurations increase and, consequently, contributions of higher configurations to the ground-state wave functions decrease. One should, however, keep in mind that for highly charged ions a finite size of the nucleus, the Breit interaction, and other higher-order magnetic interactions neglected in the present approximation may influence the values of polarizabilities. This deserves independent studies.

### Acknowledgements

This work was supported by the Polish State Committee for Scientific Research (KBN) under Grant No. PB/0916/P3/92/03. The calculations were carried out in the Computer Centre at the University of Gdańsk.

### References

1. Dalgarno, A., *Adv. Phys.* **11**, 281 (1962).
2. Teachout, R. R. and Pack, R. T., *At. Data* **3**, 37 (1971).
3. Miller, T. M. and Bederson, B., *Adv. At. Mol. Phys.* **13**, 1 (1977).
4. Miller, T. M. and Bederson, B., *Adv. At. Mol. Phys.* **25**, 37 (1988).
5. Dalgarno, A., *Proc. Roy. Soc.* **A251**, 282 (1959).
6. Kaneko, S., *J. Phys. Soc. Japan* **14**, 1600 (1959).
7. Markiewicz, E., McEachran, R. P. and Stauffer, A. D., *J. Phys.* **B14**, 949 (1981).
8. McEachran, R. P., Ryman, A. G. and Stauffer, A. D., *J. Phys.* **B10**, L681 (1977).
9. McEachran, R. P., Stauffer, A. D. and Greita, S., *J. Phys.* **B12**, 3119 (1979).
10. McEachran, R. P., Stauffer, A. D. and Brookfield, S., *J. Phys.* **B15**, 1581 (1982).
11. Kolb, D., Johnson, W. R. and Shorer, P., *Phys. Rev.* **A26**, 19 (1982).
12. Johnson, W. R., Kolb, D. and Huang, K.-N., *At. Data Nucl. Data Tables* **28**, 333 (1983).
13. Szymtkowski, R., *J. Phys.* **B24**, 3895 (1991).
14. Schiff, L. I., "Quantum Mechanics" (3rd Edn.) (McGraw-Hill, New York 1968), Chap. 13, Sec. 52.
15. Szymtkowski, R., *J. Phys.* **B26**, 535 (1993).
16. Grant, I. P., McKenzie, B. J., Norrington, P. H., Mayers, D. F. and Pyper, N. C., *Comput. Phys. Commun.* **21**, 207 (1980).
17. Szymtkowski, R., unpublished (1992).
18. Maroulis, G. and Thakkar, A. J., *J. Phys.* **B21**, 3819 (1988).
19. Muller, W., Flesch, J. and Meyer, W., *J. Chem. Phys.* **80**, 3297 (1984).
20. Lahiri, J. and Mukherji, A., *Phys. Rev.* **141**, 428 (1966).
21. Dalgarno, A. and McIntyre, H. A. J., *Proc. Phys. Soc.* **85**, 47 (1965).
22. Ray, D. and Mukherjee, P. K., *J. Phys.* **B22**, 2103 (1989).
23. Reinsch, E. A. and Meyer, W., *Phys. Rev.* **A14**, 915 (1976).
24. Bhattacharya, G. N., Mukherjee, P. K. and Roy, H. P., *Phys. Rev.* **A22**, 363 (1980).
25. Stewart, R. F., *Mol. Phys.* **30**, 745 (1975).
26. Moore, C. E., "Atomic Energy Levels" (National Bureau of Standards, Washington D.C. 1971).
27. Sadlej, A. J., Urban, M. and Gropen, O., *Phys. Rev.* **A44**, 5547 (1991).