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Static electric dipole polarizabilities for isoelectronic sequences. II. Open-shell S states[⋆,⋆⋆]

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Abstract. We present static electric dipole polarizabilities $\alpha_\mathrm{d}(Z,N)$ from numerical nonrelativistic restricted Hartree-Fock (RHF) finite-field calculations for high-spin open-shell S states ($L=0$) of atoms and isoelectronic ions with $N \leq 55$ electrons. All these S states result from one or more half-filled shells. For eight isoelectronic sequences, those with $N = 3$, 7, 11, 15, 23, 29, 33 or 41 electrons where the electronic ground state of the neutral or nearly neutral members is conserved upon increase of the nuclear charge number Z, polarizability data are given for ions with charge number $Q = Z - N$ up to $Q = 90$. In addition, these data are represented in terms of rational functions of Q (with absolute value of the relative error of the fit always below 4%). The rational functions are comparable to the classical nonrelativistic result $\alpha_\mathrm{d}(Z,1) = 4.5/Z^4 = 4.5/(Q+1)^4$ for the polarizability of the ^{2}S ground state of a hydrogen-like system. Our results also contribute to constitute a reference database (i) for algebraic approaches relying on basis functions, and (ii) for the discussion of relativistic and correlation effects on polarizabilities along isoelectronic sequences.

1 Introduction

The static electric dipole polarizability $\alpha_\mathrm{d}(Z,N)$ of an atom or atomic ion with N electrons and nuclear charge number Z is a fundamental property of that system [1–4]. In general, accurate experimental or theoretical data for this quantity are available only for neutral atoms or slightly charged ions, but not for higher or highly charged cations. For example, one way to accurately determine static electric dipole polarizabilities for slightly charged ions with N electrons from experiment is through spectroscopic studies of Rydberg states of the corresponding atom or ion with $N+1$ electrons [5,6]. The leading-order term for the attractive interaction between the Rydberg electron and the ionic core is $-(1/2)\alpha_\mathrm{d}(Z,N)/r^4$. Static electric dipole polarizabilities have found widespread application, e.g., in the modelling of potential energy curves for ground and excited electronic states of diatomic molecular ions formed from metal ions and rare gas atoms [7,8]. The lack of knowledge of polarizabilities for isoelectronic sequences of atoms and atomic ions, also with respect to their Z-expansion, is in contrast to the fact that atomic ions of almost any degree of ionization can be generated and studied rather easily with modern experimental equipment, and are of great importance in fundamental science, applied science and technology [9–11]. Data for polarizabilities along isoelectronic sequences of atoms and atomic ions, covering the full range of charge numbers $Q = Z - N$ from small values (anions, atoms or cations) up to large values (highly charged cations), are still scarce. If these sequences are studied at all, then either only some early members are considered, or Z-expansions (precisely, Z^{-1}-expansions) valid for large Z are derived [12–14].

We present here accurate data for static electric dipole polarizabilities from numerical nonrelativistic restricted Hartree-Fock (RHF) finite-field calculations for high-spin open-shell S states of atoms and members of their isoelectronic sequences. All these S states result from one or more half-filled shells. Atoms and ions with up to $N = 55$ electrons are considered, as well as eight isoelectronic sequences up to $Q = 90$. The sequences are chosen by the requirement that the electronic ground state found for small charge numbers (anionic, neutral or cationic systems) must not change upon increase of Z.

The Hartree-Fock approximation is known to have a few shortcomings: relativistic and correlation effects are omitted, and degenerate or near-degenerate states from other electron configurations, possibly gaining importance in the high-Z limit for some of the isoelectronic sequences

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included here, are excluded. However, our accurate nonrelativistic data certainly provide a firm basis of benchmark values against which results from more sophisticated methods, including the effects just mentioned, can be compared.

2 Methods

We give a very brief description of the numerical RHF method as used here to determine the energy $E_A(F)$ of some state A of an atom or atomic ion in a static electric field of strength F, mainly in order to introduce a suitable notation. Further details are given in the literature [15–18]. The representation of dipole polarizabilities along isoelectronic sequences in terms of rational functions of the total charge number Q was introduced in our previous study on closed-shell systems [19].

2.1 The energy, the induced dipole moment and the static dipole polarizability

We consider an N-electron atom or atomic ion with infinitely heavy, spin-free, point-like nucleus with charge number Z placed at the origin of the coordinate system. Its total charge number $Q = Z - N$ always fulfils the inequality $Q > -2$ (non-existence of stable free atomic dianions). In the nonrelativistic case, this system, if put in a static homogeneous electric field of strength F (oriented along the z direction), is described by the Hamiltonian (in atomic units)

$$\widehat{\mathcal{H}}(F) = \sum_{i=1}^{N} (h_i + F\, z_i) + \frac{1}{2} \sum_{i \neq j}^{N} g_{ij} \tag{1}$$

with

$$h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}, \qquad g_{ij} = \frac{1}{r_{ij}}. \tag{2}$$

For the present study, we restrict ourselves to atoms or atomic ions in a high-spin open-shell S state ($L = 0$) resulting from one or more half-filled shells. A normalized field-strength dependent total state function $\Psi_A(F)$ for such an open-shell state A can always be chosen as a single Slater determinant constructed from field-strength dependent spin orbitals, such that it transforms as an eigenfunction of the space and spin symmetry operators $\widehat{\mathcal{L}}_z$, $\widehat{\mathcal{S}}^2$ and $\widehat{\mathcal{S}}_z$ with respective eigenvalues $\Lambda = 0$, $S(S+1) > 0$ and $M_S = S$. This can be guaranteed by constructing the Slater determinant from an orthonormal set of symmetry-adapted spin orbitals $\{|\,\psi_k\,\rangle\}$ ($1 \leq k \leq k_{\max}$, $\langle\,\psi_k\,|\,\psi_l\,\rangle = \delta_{kl}$):

$$\widehat{l}_z|\,\psi_k\,\rangle = \pm\lambda_k\,|\,\psi_k\,\rangle, \qquad \widehat{s}^2|\,\psi_k\,\rangle = \tfrac{3}{4}\,|\,\psi_k\,\rangle,$$
$$\widehat{s}_z|\,\psi_k\,\rangle = \pm\tfrac{1}{2}\,|\,\psi_k\,\rangle. \tag{3}$$

Hence these spin orbitals can be written in product form as

$$\psi_{n\lambda m m_s}(\boldsymbol{r},\sigma) = e^{\mathrm{i}m\phi} f_{n\lambda}(r,\theta)\,\chi_{m_s}(\sigma), \tag{4}$$

where $f_{n\lambda}$ is the shell function, $e^{\mathrm{i}m\phi}$ is the subspecies function ($m = \pm\lambda$), and χ_{m_s} denotes the spin function (either α or β). The spatial part of the spin orbitals is then expanded with a partial wave ansatz [16]

$$e^{\mathrm{i}m\phi} f_{n\lambda}(r,\theta) = \sum_{\ell=\lambda}^{\ell_{\max}} r^{-1} P_{n\lambda\ell}(r)\, Y_{\ell m}(\theta,\phi). \tag{5}$$

For non-vanishing field strengths, this expansion, if taken as an infinite expansion, would be exact, but for every practical purpose the expansion length $\Delta\ell = \ell_{\max} - \lambda + 1$ is necessarily finite. The radial functions $P_{n\lambda\ell}$ have to obey the boundary conditions $P_{n\lambda\ell}(0) = \lim_{r\to\infty} P_{n\lambda\ell}(r) = 0$ and must be determined anew for every given field strength F and chosen expansion length $\Delta\ell$. Orbitals with the same quantum numbers n, λ are required to share the same set of radial functions, i.e., the equivalence restriction is applied.

The expectation values for energy and induced dipole moment, $E_A(F) = \langle\,\Psi_A(F)\,|\,\widehat{\mathcal{H}}(F)\,|\,\Psi_A(F)\,\rangle$ and $\mu_A(F) = \langle\,\Psi_A(F)\,|\,\sum_i z_i\,|\,\Psi_A(F)\,\rangle$, are finally expressed in terms of certain one-electron and two-electron radial integrals (see Refs. [16,17] for details). Variation of the energy expectation value with respect to the radial functions, under restriction to orthonormality of the spin orbitals, leads to coupled pseudo-eigenvalue problems for the set of radial functions associated with the shells. After discretization of the associated set of coupled ordinary second-order differential equations, the radial functions $P_{n\lambda\ell}(r)$ are obtained with numerical methods, as in the central field case [20,21].

With a complete set of radial functions $P_{n\lambda\ell}(r)$ for all shells at hand, the energy $E_A(F)$ and the induced electric dipole moment $\mu_A(F)$ at a given field strength F are easily calculated from the radial integrals mentioned above. For a many-electron atom or atomic ion, energy and induced dipole moment are even and odd functions, respectively, of the field strength,

$$\begin{aligned} E_A(F) &= \sum_{k=0}^{\infty} \frac{a_k}{(2k)!}\,F^{2k} \\ &= a_0 + \frac{a_1}{2}\,F^2 + \frac{a_2}{24}\,F^4 + \ldots, \end{aligned} \tag{6}$$

$$\begin{aligned} \mu_A(F) = \frac{dE_A}{dF} &= \sum_{k=1}^{\infty} \frac{a_k}{(2k-1)!}\,F^{2k-1} \\ &= a_1\,F + \frac{a_2}{6}\,F^3 + \ldots, \end{aligned} \tag{7}$$

where

$$a_k = \left.\frac{d^{2k-1}\mu_A}{dF^{2k-1}}\right|_{F=0} = \left.\frac{d^{2k}E_A}{dF^{2k}}\right|_{F=0}.$$

The higher-order terms in these expansions become more and more important with increasing field strength. A sufficiently large expansion length $\Delta\ell$ is required in equation (5) in order to take these terms properly into account [17].

The static electric dipole polarizability is defined as

$$\alpha_{\mathrm{d}} = -a_1 = -\left.\frac{d\mu_A}{dF}\right|_{F=0} = -\left.\frac{d^2E_A}{dF^2}\right|_{F=0}. \qquad (8)$$

Given a set of energies $E_A(F_i)$ or induced dipole moments $\mu_A(F_i)$ for various field strengths $F_i = i\,\Delta F$ ($0 \leq i \leq i_{\max}$), the polarizability is obtainable either from a linear least-squares fit of a polynomial in F to these data values, or from finite-difference expressions.

2.2 Data generation and analysis

The numerical multiconfiguration self-consistent field program for atoms in a static electric field, set up by Stiehler and Hinze [17,18], has been modified[1] and used to calculate energies and induced dipole moments at several field strengths for high-spin open-shell S states of atoms and members of their isoelectronic sequences. All considered S states result from one or more half-filled shells. The number of electrons in these systems ranges from $N = 3$ (Li sequence) to $N = 55$ (Cs, Ba^+ and La^{2+}). The isoelectronic sequences were selected by the requirement that the electronic ground state found for small values of the total charge number Q (anionic, neutral or cationic systems) must not change upon increase of Z. Eight such isoelectronic sequences, with N = 3, 7, 11, 15, 23, 29, 33 or 41 electrons, were considered for total charge numbers ranging from $Q = -1$ or $Q = 0$ up to $Q = 90$. For every single case under study, the expansion length $\Delta\ell$ in (5) was taken as three or four for all shells in a calculation. All radial functions $P_{n\lambda\ell}(r)$ present in the set of expansions (5) were represented with n = 800, 1600, 3200 or 6400 equidistant points on a transformed radial grid. The field strength F was increased until the magnitude of the induced dipole moment reached a value of $\mu \approx 0.02$ a.u. In this way, typically $i_{\max} \approx 20$ values for energy $E_A(F_i)$ and induced dipole moment $\mu_A(F_i)$ at increasing field strengths were obtained. The relations (8) were then used to calculate the polarizability.

Finally, for each of the eight isoelectronic sequences (N constant) a rational function

$$\widetilde{\alpha}_{\mathrm{d}}(Q) = \frac{1}{(Q-Q_0)^n}\frac{F_k(Q)}{G_l(Q)} \qquad (Q > Q_0),$$
$$F_k(Q) = \sum_{i=0}^{k} f_i Q^i, \qquad G_l(Q) = \sum_{j=0}^{l} g_j Q^j, \qquad (9)$$

was fitted to the set of polarizabilities $\alpha_{\mathrm{d}}(Z,N) = \alpha_{\mathrm{d}}(Z-N) = \alpha_{\mathrm{d}}(Q)$. Details of the procedure adopted to determine the position Q_0 and the order n of the pole defining a lower boundary for Q, and of the non-linear least-squares fit used to fix the polynomial coefficients f_i and g_j are given in our previous study [19]. We assume that none of these polynomial coefficients vanishes.

3 Results

We present in Tables 1 and 2 our results for the static dipole polarizabilities $\alpha_{\mathrm{d}}(Z,N)$ from numerical nonrelativistic restricted Hartree-Fock (RHF) finite-field calculations for high-spin open-shell S states of atoms and isoelectronic ions. In total, we considered 186 systems. All values are given in atomic units, conversion to SI units is easily achieved with the relation 1 a.u. $= e^2a_0^2/E_{\mathrm{h}} = 1.64877727 \times 10^{-41}\ (\mathrm{Cm})^2\ \mathrm{J}^{-1}$ [22] (e is the elementary charge, a_0 the Bohr radius, E_{h} the Hartree energy unit, see [4] for an overview of other units used for the dipole polarizability). In addition, a table with field-free numerical RHF energies of the atoms and isoelectronic ions is provided as electronic-only material[2].

3.1 Atoms and ions with small charge number

The entries of Table 1 are arranged according to their groups in the periodic table. In each row of the table, the number of electrons N is given, followed by a name for the sequence, by the electron configuration and by the LS term considered. Then follow our results for the static polarizabilities of the atom and ions with small charge numbers ($Q = -1, 0, 1, 2$). A checkmark sign in the last column indicates availability of data for the isoelectronic sequence in Table 2.

Data for anions are given only for anions of atoms from group 14 (C^-, Si^-, Ge^-, Sn^-) and for the ions Cr^- ($N = 25$), Nb^- ($N = 42$) and Mo^- ($N = 43$). In all other cases of anionic systems, we did not succeed to determine the static polarizability. Reasons for this failure include, e.g., severe convergence problems in the SCF procedure or, if SCF convergence could be achieved, positive orbital energies already in field-free calculations (essentially indicating an unbound single-particle state leading to autoionization).

We believe our values, derived from field-strength dependent energies and induced dipole moments, to be accurate enough to allow six digits to be given. As far as data for comparison are available, our values are in full accord with the most recent ones from numerical RHF calculations [17,23]. Together with Table 1, we also provide a survey of literature data obtained from numerical or algebraic RHF calculations, or from time-dependent HF calculations in the static limit ($\omega = 0$). In almost all cases, these previously published values compare very well with our new values (differences are typically below 1%). We can thus conclude that the specially designed basis sets used in those studies work very well and lead to the desired results for α_{d} close to its Hartree-Fock limit value. The early and extensive work by Fraga et al. [24–26] deserves mention because it provides static electric dipole polarizabilities for all atoms, from helium to nobelium, and several early members of their isoelectronic

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[1] V. Koch, modified version of the numerical MCSCF program for atoms in a static electric field [18] (unpublished).

[2] Electronic-only material: Table with field-free numerical RHF energies for atoms and isoelectronic ions (see ** on the first page).

Table 1. Six-digit static electric dipole polarizabilities $\alpha_{\mathrm{d}}(Z,N)$ (in a.u.[†]) from numerical nonrelativistic RHF finite-field calculations for high-spin open-shell S states ($L = 0$) of atoms and ions with small charge number $Q = Z - N$ (electron configurations as indicated).

N	Sequence name, electron configuration and state	$Q = -1$	$Q = 0$	$Q = +1$	$Q = +2$	$Q > 2$
3	Li [He] $2s^1$ ^{2}S	–	170.120[a1]	24.9596[b1]	7.95019	✓[‡]
11	Na [Ne] $3s^1$ ^{2}S	–	190.503[a2]	38.8547[b2]	15.4462[c1]	✓
19	K [Ar] $4s^1$ ^{2}S	–	417.811[a3]	98.6261[b3]	42.7804	
37	Rb [Kr] $5s^1$ ^{2}S	–	524.878[a4]	132.096[b4]	60.2147	
55	Cs [Xe] $6s^1$ ^{2}S	–	807.639[a5]	213.398[b5]	100.248	
7	N [He] $2s^2$ $2p^3$ ^{4}S°	51.6627[d1]	7.35815[e1]	2.67238	1.28727	✓
15	P [Ne] $3s^2$ $3p^3$ ^{4}S°	133.754[d2]	25.4694[e2]	10.9397	5.99168	✓
33	As [Ar] $3d^{10}$ $4s^2$ $4p^3$ ^{4}S°	148.786	30.4691[e3]	14.4328	8.64222	✓
51	Sb [Kr] $4d^{10}$ $5s^2$ $5p^3$ ^{4}S°	175.683	45.4680[e4]	23.6485	15.0553	
23	Cr^+ [Ar] $3d^5$ ^{6}S	–	68.3893	8.96554[f1]	3.19986[g1]	✓
41	Mo^+ [Kr] $4d^5$ ^{6}S	–	67.5329	16.7455	7.67505	✓
24	Cr [Ar] $3d^5$ $4s^1$ ^{7}S	–	112.881[h1]	40.4562	20.5349	
42	Mo [Kr] $4d^5$ $5s^1$ ^{7}S	1045.37	127.723	53.8296	29.9529	
25	Mn [Ar] $3d^5$ $4s^2$ ^{6}S	977.235	90.1395[i1]	36.4941	20.0647	
43	Tc [Kr] $4d^5$ $5s^2$ ^{6}S	979.527	115.925	52.2363	30.7953	
29	Cu [Ar] $3d^{10}$ $4s^1$ ^{2}S	–	77.1914[j1]	25.3019[k1]	12.9081	✓
47	Ag [Kr] $4d^{10}$ $5s^1$ ^{2}S	–	105.545[j2]	37.9484[k2]	20.7683	

[†] Conversion to SI units: 1 a.u. = $1.64877727 \times 10^{-41}$ $(\mathrm{Cm})^2$ J^{-1}.

[‡] The checkmark sign indicates availability of data for the isoelectronic sequence, see Table 2.

Literature values for $\alpha_{\mathrm{d}}(Z,N)$ from either numerical or algebraic nonrelativistic RHF calculations or from time-dependent HF calculations in the static limit (basis sets used were assumed to be of near-Hartree-Fock-limit quality with respect to this property):

[a1] 170.1 [16], 171.6 [28], 170.1 [17], 169.5 [29], 169.50 [30], 170.11998 [23];
[a2] 191.2 [31], 190.9 [28], 190.50 [17], 190.5 [29], 190.49 [30], 190.49 [32];
[a3] 416.1 [33], 416.4 [28], 417.8 [17], 416.7 [29], 416.60 [30];
[a4] 523.7 [28], 523.7 [33], 524.2 [29], 522.39 [30];
[a5] 806.8 [29], 806.81 [30];
[b1] 24.25 [28], 24.71 [29];
[b2] 38.90 [31], 38.84 [28], 38.91 [29];
[b3] 98.0 [28], 98.27 [29], 98.64 [34];
[b4] 130.5 [28], 131.6 [29], 132.15 [34];
[b5] 211.6 [29], 213.47 [34];
[c1] 15.45 [31];
[d1] 48.2 [35], 50.1 [36];
[d2] 129.9 [35], 136.3 [37];
[e1] 7.436 [16], 7.3 [38], 7.3581 [17], 7.34 [39], 7.3556 [40];
[e2] 25.08 [41], 25.2 [38], 25.469 [17], 25.47 [42];
[e3] 30.469 [17];
[e4] 45.49 [43];
[f1] 9.00 [44];
[g1] 3.23 [44];
[h1] 112.88 [17], 106.26 [45], 112.9 [46];
[i1] 90.139 [17], 89.2 [45], 90.6 [46];
[j1] 73.56 [47], 77.190 [17], 76.4 [48], 76.18 [49], 73.46 [45];
[j2] 104.0 [48], 105.4 [47];
[k1] 24.83 [50];
[k2] 37.12 [50].

Table 2. Six-digit static electric dipole polarizabilities $\alpha_\mathrm{d}(Z,N)$ (in a.u.[†]) for isoelectronic sequences of high-spin open-shell S states ($L=0$) of atoms and ions with N electrons (from numerical nonrelativistic RHF finite-field calculations, charge number $Q=Z-N$, electron configurations and LS states as in Tab. 1, see Fig. 1 for a graphical representation of the data).

Q	$N=3$ (Li $2s^1$ ^{2}S)	$N=7$ (N $2p^3$ ^{4}S°)	$N=11$ (Na $3s^1$ ^{2}S)	$N=15$ (P $3p^3$ ^{4}S°)	$N=23$ (Cr$^+$ $3d^5$ ^{6}S)	$N=29$ (Cu $4s^1$ ^{2}S)	$N=33$ (As $4p^3$ ^{4}S°)	$N=41$ (Mo$^+$ $4d^5$ ^{6}S)
−1	—	5.16627(+1)[‡]	—	1.33754(+2)	—	—	1.48786(+2)	—
0	1.70120(+2)	7.35815	1.90503(+2)	2.54694(+1)	6.83893(+1)	7.71914(+1)	3.04691(+1)	6.75329(+1)
+1	2.49596(+1)	2.67238	3.88547(+1)	1.09397(+1)	8.96554	2.53019(+1)	1.44328(+1)	1.67455(+1)
+2	7.95019	1.28727	1.54462(+1)	5.99168	3.19986	1.29081(+1)	8.64222	7.67505
+3	3.49174	7.20609(−1)	7.94407	3.71614	1.65783	7.85027	5.79645	4.51407
+4	1.83368	4.44155(−1)	4.69443	2.49097	1.02409	5.26093	4.16134	3.01733
+5	1.07970	2.92974(−1)	3.02916	1.76229	6.97544(−1)	3.75280	3.12760	2.17587
+6	6.88505(−1)	2.03306(−1)	2.07804	1.29771	5.05104(−1)	2.79716	2.43019	1.64913
+7	4.65632(−1)	1.46764(−1)	1.49172	9.85796(−1)	3.81401(−1)	2.15431	1.93689	1.29453
+8	3.29453(−1)	1.09358(−1)	1.10910	7.67783(−1)	2.96951(−1)	1.70207	1.57516	1.04307
+9	2.41596(−1)	8.36347(−2)	8.48096(−1)	6.10399(−1)	2.36705(−1)	1.37262	1.30222	8.57650(−1)
+10	1.82396(−1)	6.53698(−2)	6.63615(−1)	4.93722(−1)	1.92258(−1)	1.12579	1.09144	7.16732(−1)
+20	2.68217(−2)	1.13598(−2)	1.18246(−1)	1.05170(−1)	4.27467(−2)	2.66860(−1)	2.93978(−1)	1.95548(−1)
+30	8.40493(−3)	3.77282(−3)	4.00442(−2)	3.83525(−2)	1.58763(−2)	1.03631(−1)	1.21377(−1)	8.24044(−2)
+40	3.64778(−3)	1.68545(−3)	1.81206(−2)	1.80749(−2)	7.52274(−3)	5.08251(−2)	6.17696(−2)	4.25711(−2)
+50	1.89991(−3)	8.93019(−4)	9.68682(−3)	9.91364(−3)	4.12579(−3)	2.86448(−2)	3.56921(−2)	2.48629(−2)
+60	1.11215(−3)	5.28679(−4)	5.77199(−3)	6.01250(−3)	2.49628(−3)	1.77170(−2)	2.24771(−2)	1.57789(−2)
+70	7.06133(−4)	3.38358(−4)	3.71230(−3)	3.91721(−3)	1.62095(−3)	1.17146(−2)	1.50664(−2)	1.06374(−2)
+80	4.75980(−4)	2.29430(−4)	2.52690(−3)	2.69272(−3)	1.11022(−3)	8.14587(−3)	1.05894(−2)	7.50904(−3)
+90	3.35905(−4)	1.62653(−4)	1.79697(−3)	1.92978(−3)	7.92759(−4)	5.89173(−3)	7.72545(−3)	5.49670(−3)

[†] Conversion to SI units: 1 a.u. = 1.64877727 × 10^{-41} (Cm)^2 J^{-1}.

[‡] The number in brackets following the entries indicates the power of ten by which the entry is to be multiplied.

sequences. Based on an average-energy-of-configuration approach, both ground-state and excited-state electron configurations were considered. Their values, calculated from the Pople-Schofield [27] variational-perturbation expression for α_d, are given to three or four digits, in units of Å^3 (1 Å^3 = 6.74833458 a.u.). Only very few of their values deviate little from the more accurate later and our present results. The following data by Fraga and coworkers deviate by less than 5% from our state-specific RHF values: $\alpha_\mathrm{d}(\mathrm{N}) = 1.14$ Å^3 = 7.69 a.u. ($N=7$), $\alpha_\mathrm{d}(\mathrm{Cl}^{2+}) = 0.913$ Å^3 = 6.16 a.u. ($N=15$) and $\alpha_\mathrm{d}(\mathrm{Cr}^{+}) = 1.39$ Å^3 = 9.38 a.u. ($N=23$).

3.2 Isoelectronic sequences

We present in Table 2 static dipole polarizabilities $\alpha_\mathrm{d}(Z,N)$ for additional members of eight isoelectronic sequences with $N = 3, 7, 11, 15, 23, 29, 33$ and 41 electrons. With only two exceptions, the selected high-spin open-shell S states (already indicated in Tab. 1) are ground states for all atoms and ions along these isoelectronic sequences. The sole exceptions are V ($N=Z=23$, $3d^5$) and Nb ($N=Z=41$, $4d^5$), for which the selected ^{6}S states are excited electronic states.

In an attempt to find a compact mathematical expression for the static polarizabilities $\alpha_\mathrm{d}(Z,N)$ for an isoelectronic sequence (N constant), we introduced a rational function representation $\widetilde{\alpha}_\mathrm{d}(Q)$ in our previous study on closed-shell systems [19]. The accurate analytic representation of the polarizability data for nine isoelectronic sequences of closed-shell systems required several different rational function representations (9), differing, e.g., in the order n of the pole at Q_0 and in the degrees of the numerator and denominator polynomials.

In the present study, just a single type of rational function $\widetilde{\alpha}_\mathrm{d}(Q)$ was found to suffice to provide accurate analytic representations of the calculated polarizabilities $\alpha_\mathrm{d}(Z,N)$ (N constant) for all eight isoelectronic sequences:

$$\widetilde{\alpha}_\mathrm{d}(Q) = \frac{1}{(Q-Q_0)^2}\,\frac{f_0 + f_1 Q}{g_0 + g_1 Q + Q^2} \qquad (Q > Q_0). \quad (10)$$

This expression has a pole of order $n=2$ at Q_0 ($-2 < Q_0 < 0$) and behaves as f_1/Q^3 for $Q \to \infty$. The eight parameter sets, obtained from the polarizability data analysis as described above, are collected in Table 3, together with the maximum absolute value of the relative errors $\Delta_k = \widetilde{\alpha}_\mathrm{d}(Q_k)/\alpha_\mathrm{d}(Q_k) - 1$ (the index k runs over the data points, i.e., the members of an isoelectronic sequence). The data points $\alpha_\mathrm{d}(Z,N)$ themselves and their analytic representation $\widetilde{\alpha}_\mathrm{d}(Q)$ for all eight isoelectronic sequences are shown in Figure 1.

Even though the functions $\widetilde{\alpha}_\mathrm{d}(Q)$ are results of a fitting procedure, rather than exact closed-form expressions, they are qualitatively comparable to the polarizability of a hydrogen-like system in its ^{2}S ground state, $\alpha_\mathrm{d}(Z,1) = 4.5/Z^4 = 4.5/(Q+1)^4$. The different behaviour for $Q \to \infty$ ($\widetilde{\alpha}_\mathrm{d}(Q) \sim Q^{-3}$ vs. $\alpha_\mathrm{d}(Z,1) \sim Q^{-4}$) is due to

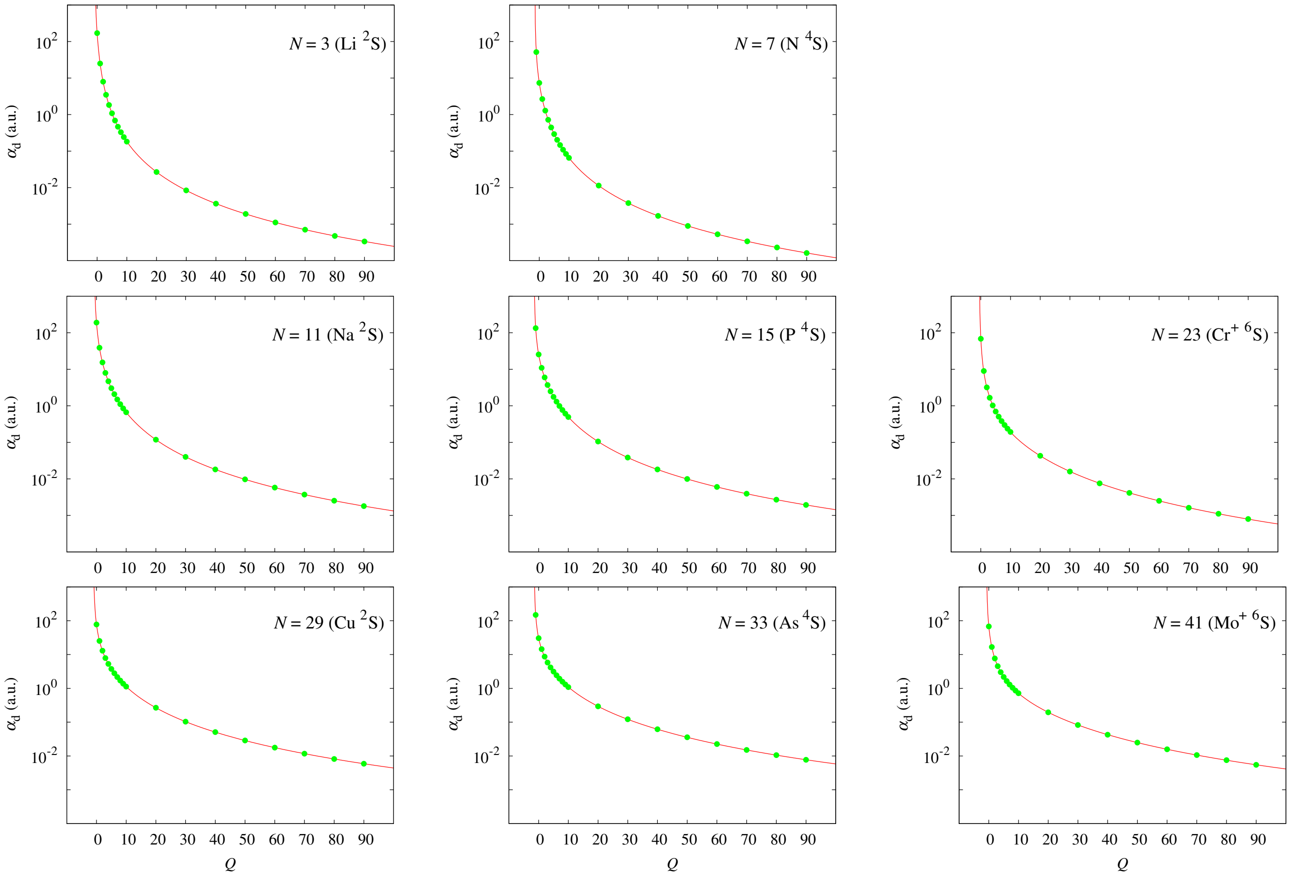

Fig. 1. Static electric dipole polarizabilities $\alpha_\mathrm{d}(Z, N)$ (in a.u.) for isoelectronic sequences of high-spin open-shell S states of atoms and ions as functions of total charge number $Q = Z - N$. Data from Table 2 (points) and their analytic rational function representations (10) with parameters from Table 3 (curves).

Table 3. Parameters of the analytical representation (10) for $\alpha_\mathrm{d}(Q)$ for eight isoelectronic sequences ($Q = Z - N$, N constant, $\max|\Delta|$ in %).

N	Q_0	f_0	f_1	g_0	g_1	$\max\lvert\Delta\rvert$
3	−0.894708	1263.13	254.504	9.27530	6.66255	0.005
7	−1.57690	395.998	128.565	21.6045	7.04860	0.32
11	−0.87115	7756.26	1451.72	53.6502	13.0317	0.014
15	−1.58020	3553.58	1673.21	55.8193	15.0550	0.16
23	−0.535847	8643.64	627.057	437.329	16.9038	3.8
29	−1.11369	14021.3	5584.05	146.507	25.5234	0.24
33	−1.56819	17804.0	7940.58	237.147	32.7723	0.20
41	−0.878531	29365.5	5624.96	562.203	35.1152	1.1

the fact that in the many-electron ions additional subshells with the same principal quantum number n become degenerate with the open shells already present at small Q. This is in accord with a general result derived from double perturbation theory [51].

4 Summary and conclusions

We present here nonrelativistic static electric dipole polarizabilities $\alpha_\mathrm{d}(Z, N)$ for high-spin open-shell S states ($L = 0$) of atoms and isoelectronic ions with up to $N = 55$ electrons, including members of eight isoelectronic sequences with total charge numbers ranging from $Q = -1$ up to $Q = 90$. Our accurate data, given to six digits in Tables 1 and 2, were obtained from numerical nonrelativistic RHF finite-field calculations according to the method outlined in Section 2. For the polarizabilities of the eight isoelectronic sequences, accurate rational function representations $\widetilde{\alpha}_\mathrm{d}(Q)$ were determined by a non-linear least-squares fit, with maximum absolute value of their relative error $\Delta = \widetilde{\alpha}_\mathrm{d}/\alpha_\mathrm{d} - 1$ being always less than 4%. All eight functions $\widetilde{\alpha}_\mathrm{d}(Q)$ show a pole of order $n = 2$ at some suitably determined lower boundary Q_0 ($-2 < Q_0 < 0$) and decrease monotonously according to a Q^{-3}-law for large values of Q, see Figure 1.

The rational functions $\widetilde{\alpha}_{\mathrm{d}}(Q)$ from (10) can be considered as analogues of the classical nonrelativistic result $\alpha_{\mathrm{d}}(Z,1) = 4.5/Z^4 = 4.5/(Q+1)^4$ for the polarizability of the ^{2}S ground state of a hydrogen-like system.

The results presented here also contribute, together with the data of our previous study on polarizabilities of atoms and ions from closed-shell isoelectronic sequences [19], to constitute a set of reference data (i) for algebraic approaches relying on basis functions; and (ii) for the discussion of relativistic and correlation effects on polarizabilities along isoelectronic sequences.

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