Multipole Polarizabilities from Hartree-Fock Densities by Statistical Perturbation Theory, a Semiempirical Approach

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A statistical variation-perturbation method is used in the derivation of multipole polarizabilities from Hartree-Fock electron densities. A quantum correction of the kinetic energy expressions takes into account the exponential decrease of the electron density in the outer part of the atom. The method is called semiempirical because of the still unsolved problem of the kinetic energy in the statistical theory of the atom. The results are compared to the best available experimental and theoretical values of dipole- and quadrupole-polarizabilities and show agreement within approximately 10—15 percent. They are lower than Hartree-Fock perturbation results. As the numerical calculations are reduced to single integrations, the mathematical labor is considerably reduced. In an appendix dipole polarizabilities are calculated in the framework of the Gombás model including exchange and correlation for ionization degrees from zero to six.

1. Introduction

Multipole polarizabilities are important second order atomic properties finding wide applications in atomic interaction processes in gases, liquids and solids. Though calculations of Hartree-Fock wave functions with relativistic and correlation corrections are standard methods, the calculation of multipole polarizabilities still presents numerical difficulties, as was shown by Dalgarno[1] in his comprehensive review on polarizabilities.

Thus, coupled Hartree-Fock[1] (CHF) and many body Bruekner-Goldstone[2] (BG) perturbation theory is applied only to few atoms and ions. On the other hand easier methods like the Pople-Schofield[1] technique or uncoupled Hartree-Fock[1] (UHF) methods which were used for a large number of atoms and ions were criticized in a recent comprehensive data collection by Teachout and Pack[3]. They remarked that there can be deviations from the best experimental values of a factor 2. An easy method giving reliable multipole polarizabilities will therefore be needed.

The technique presented here will be shown to meet this demand. In 1958 Gombás developed a statistical variation-perturbation method including quantum corrections of the kinetic energy and applied it to the calculation of dipole polarizabilities[4, 5]. His results were encouraging for Ar, where he used a Hartree-Fock electron density. The complete agreement was fortuitous because of an error in his energy expression. His technique will be worked out for static field polarizabilities of higher order. Hartree-Fock electron densities which are assumed to be spherical will be used. Though no experimental or adjustable parameters are applied we call the method semiempirical because of the following reasons:

(i) The statistical theory is unable to give the atomic shell structure,

(ii) the mixing of statistical and Hartree-Fock methods is only justified by the success of giving multipole polarizabilities of good accuracy,

(iii) the quantum corrections to the Thomas-Fermi-theory are not unambigous for atoms as will be pointed out in Section 2.

As there exist excellent monographs[6] and reviews[7, 8] on the statistical theory of matter we shall give references to original papers only for those later than 1956.

The plan of the paper is the following: After a brief sketch of the present state of the kinetic energy problem in Section 2, the relevant formulae of statistical perturbation theory are summarized in Section 3. Numerical results are given in Section 4. Section 5 discusses limitations and further applications.

2. The Kinetic Energy of the Statistical Atom

In the original Thomas-Fermi(TF)-theory the kinetic energy density is given by

$$E_k = \varkappa_k \varrho^{5/3}, \quad \varkappa_k = 0.3\,(3\pi^2)^{2/3}\,\hbar^2/m, \quad \varrho = \text{density}. \tag{1}$$

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Weizsäcker[6] introduced a correction of the form

$$E_{\mathrm{i}} = \xi \frac{\hbar^2}{8\,m} \frac{(\nabla \varrho)^2}{\varrho} = \xi\, \varkappa_{\mathrm{i}} \frac{(\nabla \varrho)^2}{\varrho}\,, \tag{2}$$

$\varkappa_{\mathrm{i}} = \hbar^2/8\,m$, i = inhomogeneous, ξ = parameter, which was investigated by a number of authors[7, 8]. Later work beginning with the treatment of Dirac's density matrix by Kirzhnits[9] is cited in the articles by Goodisman[10] and Baltin[11]. We shall, therefore, only sketch some recent results to give a justification of our choice of ξ.

Several authors found that $\xi = 1/9$, the value which was derived by Kirzhnits[9], is correct, but numerical results with this value were poor. The discussion of the kinetic energy expression was renewed by Yonei and Tomishima[12, 13], who investigated numerically the statistical equation of the atom with variable ξ. They found for the energy, that $\xi = 0.2$ gives the best agreement with Hartree-Fock results but they remarked that the density in the outer part of the atom is better approximated with $\xi = 1$. In a systematic investigation of the inhomogeneous electron gas Kohn and coworkers[14, 15] showed that $\xi = 1/9$ is valid for slowly varying density, a result which was further elaborated by Stoddart, Beattie, and March[26]. Bruekner and Ma[17] used linear response theory and found for slowly varying density the same result. Goodisman[10] used a WKB-type approach and suggested that the full Weizsäcker-correction should be used throughout along with the Thomas-Fermi-term. He introduced a cutoff near the nucleus such that the 1s-density no longer dominated the total density. Baltin[11] in a somewhat different approach found for small y

$$E_{\mathrm{k}} = E_{\mathrm{k}}^{\mathrm{TF}} + \frac{5}{9} \frac{\hbar^2}{8m} \frac{(\nabla \varrho)^2}{\varrho} + \frac{2}{3} \frac{\hbar^2}{8m} \frac{(\nabla \varrho)^2}{\varrho} \sin\left[\frac{2\,(3\,\pi^2)^{1/3}\,\varrho^{4/3}}{|\nabla \varrho|}\right],$$

$$y = |\nabla \varrho|^{1/2}\,\varrho^{-2/3} \tag{3}$$

which in the limit of $y \to \infty$ becomes the Weizsäcker term alone. We conclude that $\xi = 1/9$ is valid only for slowly varying density and cannot be used for the exponentially decaying electron density in the outer part of the atom. In the following calculations we shall use the Thomas-Fermi and the Weizsäcker term with $\xi = 1$, which seems to be reasonable from Goodisman's[10] and Baltin's[11] work. For comparison we shall give the results for the rare gases with $\xi = 0.2$ [Table 3] showing that the results are unreasonably high.

3. Formulae of Statistical Perturbation Theory Applied to Multipole Polarizabilities

The variation-perturbation theory for the statistical atom was derived by Gombás[4]. As the original work is not always available the relevant formulae are sketched and generalized for multipole polarizabilities.

For the density ϱ, weakly perturbed by an external field, the perturbed density ϱ' is

$$\varrho' = \varrho + \delta\varrho;\ \int \delta\varrho\, \mathrm{d}v = 0\,. \tag{4}$$

From the Fermi-Almadi model (see Gombás[6]) follows a possible form of the density variation $\delta\varrho$

$$\delta\varrho = \lambda\varrho\,(v_{\mathrm{s}} - v_0)/V^* \tag{5}$$

with λ = variation parameter, v_{s} = perturbing potential,

$$v_0 = [\int \varrho\, v_{\mathrm{s}} (V^*)^{-1}\, \mathrm{d}v] / \int \varrho (V^*)^{-1}\, \mathrm{d}v$$
$$V^* = \text{average Fermi-Amaldi potential.} \tag{6}$$

The energy of the perturbed atom is expanded to second order in λ leading with the abbreviation

$$s = (V^*)^{-1}\,(v_{\mathrm{s}} - v_0) \tag{7}$$

to the first and second order perturbation energies ΔE_1 and ΔE_2.

$$\Delta E_1 = -e \int v_{\mathrm{s}}\, \varrho\, \mathrm{d}v\,, \tag{8}$$

$$\Delta E_2 = -W_{\mathrm{s}}\, \lambda + (W_{\mathrm{k}} + W_{\mathrm{i}} + W_{\mathrm{p}} - W_{\mathrm{a}})\, \lambda^2 \tag{9}$$

where W_{s}, W_{k}, W_{i}. W_{p}, W_{a} are the following integrals

$$W_{\mathrm{s}} = e \int v_{\mathrm{s}}\, s\, \varrho\, \mathrm{d}v; \tag{10}$$

$$W_{\mathrm{k}} = (5/9)\, \varkappa_{\mathrm{k}} \int \varrho^{5/3}\, s^2\, \mathrm{d}v; \tag{11}$$

$$W_{\mathrm{p}} = \frac{e^2}{2} \int\!\!\int \frac{s(\boldsymbol{r})\, s(\boldsymbol{r}')\, \varrho(\boldsymbol{r})\, \varrho(\boldsymbol{r}')\, \mathrm{d}v\, \mathrm{d}v'}{|\boldsymbol{r} - \boldsymbol{r}'|}\,; \tag{12}$$

$$W_{\mathrm{a}} = (2/9)\, \varkappa_{\mathrm{a}} \int \varrho^{4/3}\, s^2\, \mathrm{d}v;\ \varkappa_{\mathrm{a}} = (3/4)\,(3/\pi)^{1/3}\, e^2; \tag{13}$$

$$W_{\mathrm{i}} = \xi\, \varkappa_{\mathrm{i}} \int \varrho\, (\operatorname{grad} s)^2\, \mathrm{d}v\,. \tag{14}$$

The variation parameter λ is fixed by the minimum condition for the energy

$$\mathrm{d}E/\mathrm{d}\lambda = 0\,. \tag{15}$$

Analogous to the Rayleigh-Schrödinger theory the first order energy change is the average of the perturbing potential. The second order perturbation energy is

$$\Delta E_2 = -W_{\mathrm{s}}^2 / [4 (W_{\mathrm{k}} + W_{\mathrm{i}} + W_{\mathrm{p}} - W_{\mathrm{a}})] = -(1/2)\, \alpha(2^L)\,. \tag{16}$$

Dalgarno[1] gave the relation between multipole polarizabilities and second order perturbation theory. Higher order perturbation theory will lead to hyperpolarizabilities. If the source of the perturbing field is a point charge e, a distance R apart, then the interaction between the N-electron atom and the point charge is

$$V = Z\,e^2/R - \sum_{i=1}^{N} e/\boldsymbol{r}_i' \tag{17}$$

Z = atomic charge, $\boldsymbol{r}_i'$ = distance between electron i and point charge. The $\boldsymbol{r}_i'$ are replaced by the $\boldsymbol{r}_i$ centred at the nucleus. The customary multipole expansion is performed:

$$V = \frac{Z\,e^2}{R} - e \sum_{L=1}^{\infty} \sum_{i=1}^{N} (r_i^L/R^{L+1})\, P_L(\cos\Theta_i)\,. \tag{18}$$

The perturbing potential is now for each multipole order L

$$v_s = -\sum_{i=1}^{N} r_i^L\, P_L(\cos\Theta_i) \tag{19}$$

where $P_L(\cos\Theta_i)$ are Legendre polynomials of order L.

The perturbing potential can be introduced in (10) – (14) for each multipole order separately leading to the multipole polarizabilities. The integrals are up to $L = 3$

$$W_\mathrm{i}(\mathrm{D}) = (4\pi\varkappa_\mathrm{i}/3)\int_0^\infty \varrho\left[\frac{3\,r^2}{V^{*2}} - \frac{2\,r^3}{V^{*3}}\left(\frac{\mathrm{d}V^*}{\mathrm{d}r}\right) + \frac{r^4}{V^{*4}}\left(\frac{\mathrm{d}V^*}{\mathrm{d}r}\right)^2\right]\mathrm{d}r\,, \tag{20}$$

$$W_\mathrm{i}(\mathrm{Q}) = (4\pi\varkappa_\mathrm{i}/5)\int_0^\infty \varrho\left[\frac{10\,r^4}{V^{*2}} - \frac{4\,r^5}{V^{*3}}\left(\frac{\mathrm{d}V^*}{\mathrm{d}r}\right) + \frac{r^6}{V^{*4}}\left(\frac{\mathrm{d}V^*}{\mathrm{d}r}\right)^2\right]\mathrm{d}r\,, \tag{21}$$

$$W_\mathrm{i}(\mathrm{O}) = (4\pi\varkappa_\mathrm{i}/7)\int_0^\infty \varrho\left[\frac{21\,r^6}{V^{*2}} - \frac{6\,r^7}{V^{*3}}\left(\frac{\mathrm{d}V^*}{\mathrm{d}r}\right) + \frac{r^8}{V^{*4}}\left(\frac{\mathrm{d}V^*}{\mathrm{d}r}\right)^2\right]\mathrm{d}r \tag{22}$$

with

$$V^* = \frac{Z\,e}{r} - \left(\frac{N-1}{N}\right) e\left[\frac{4\pi}{r}\int_0^r \varrho(r')\,r'^2\,\mathrm{d}r' + 4\pi\int_r^\infty \varrho(r')\,r'\,\mathrm{d}r'\right], \tag{23}$$

$$\frac{\mathrm{d}V^*}{\mathrm{d}r} = -\frac{Z\,e}{r^2} + \left(\frac{N-1}{N}\right)\left[\frac{4\pi\,e}{r^2}\int_0^r \varrho(r')\,r'^2\,\mathrm{d}r'\right], \tag{24}$$

$$W_\mathrm{s} = [4\pi/(2\,L+1)]\,e^2 \int_0^\infty \varrho(r)\,r^{2L+2}(V^*)^{-1}\,\mathrm{d}r\,, \tag{25}$$

$$W_\mathrm{k} = [20\,\pi\,\varkappa_\mathrm{k}/9\,(2\,L+1)] \int_0^\infty [\varrho(r)]^{5/3}\,r^{2L+2}\,(V^*)^{-2}\,\mathrm{d}r\,, \tag{26}$$

$$W_\mathrm{p} = [4\pi/(2\,L+1)]^2\,e^2 \int_0^\infty \varrho(r)\,V^*(r)^{-1}\,r\left[\int \varrho(r')\,V^*(r')^{-1}\,r'^{2L+2}\,\mathrm{d}r'\right]\mathrm{d}r\,, \tag{27}$$

$$W_\mathrm{a} = [8\,\pi\,\varkappa_\mathrm{a}/9\,(2\,L+1)] \int_0^\infty [\varrho(r)]^{4/3}\,r^{2L+2}\,(V^*)^{-2}\,\mathrm{d}r\,. \tag{28}$$

The consistent way would be the calculation of $\varrho(r)$ from the Thomas-Fermi-Dirac-Weizsäcker (TFDW-) equation, insertion into (10) – (14) and integration. Solving the TFDW-equation is not easy as was shown by Gombás[6] and by Yonei and Tomishima[12, 13]. Furthermore it was already mentioned in the introduction that the statistical density differs from the Hartree-Fock density in several respects leading to unrealistic polarizabilities, which was shown by Gombás[5] for the rare gases. His results are not correct, as the second term in (20) is missing. He suggested to use Hartree-Fock densities in the calculations and showed for Ar that the result is comparable to the experimental result. We follow his suggestions and use Hartree-Fock (HF) densities from the literature. Because of the mixture of HF densities and Thomas-Fermi-Dirac-Weizsäcker-perturbation-theory we call this semiempirical method TFDW-HF.

4. Multipole Polarizabilities

4.1. The two Electron Isoelectronic Series

We seperate the results for the two-electron series, as for one and two electrons, the kinetic energy is identical with the Weizsäcker-term alone. The expression for the perturbed energy of the second order is:

$$\alpha = W_s{}^2/2(W_i + \tfrac{1}{2} W_p) \, . \qquad (29)$$

The result of the calculation up to $L = 4$ is given in Table 1, together with the recent results by Stewart and Webster [18]. It is not surprising that the two electron series can be written as an approximate hydrogenic series (see 4.3 below).

4.2. Many-electron Atoms and Ions

Using Hartree-Fock electron densities from the literature, which are assumed to be spherical, Table 2 is calculated. For comparison the best available experimental and theoretical dipole- and the best theoretical quadrupole polarizabilities are given. Less reliable values according to the remarks of Teachout and Pack [3] are given in bracketts. Comparing the results one sees that the dipole values are lower, whereas the quadrupole values are in good agreement.

4.3. Some Qualitative Checks

More than forty years ago Pauling [19] calculated polarizabilities with a hydrogenic model which were in fair agreement with experimental results. He suggested that dipole polarizabilities should vary inversely as the fourth power of the screened nuclear charge. The so called "Pauling plot" was used often as a check of consistency for isoelectronic series. For multipole polarizabilities in $[\text{Å}^{2L+1}]$ for a hydrogenic system it is:

$$\alpha(2^L) = 0.529^{2L+1} \, L^{-1} \, 2^{-2L} (L+2)(2L+1)! \, (Z-\sigma)^{-(2L+2)} = (A/2)(Z-\sigma)^{-(2L+2)} \qquad (30)$$

where σ is a screening constant. It could be expected that this expression is valid for effective one- and two-electron systems but it is very surprising that is applies to the three- and four electron isoelectronic series, too. This can be seen both from CHF-values and from the results given in Table 2. We plotted the appropriate inverse powers of the multipole polarizabilities for two-, three- and four-electron systems against the nuclear charge. Though the CHF- and TFDW-HF-plots have different slopes they are consistent.

A second check of our choice of ξ in the kinetic energy expression is by solving the perturbation

Table 1. Multipole polarizabilities by the TFDW-HF-method (two electron systems).

TF D, TF Q, TF O, TF H   Dipole, quadrupole, octopole, hexadecapole polarizabilities by the TFDW-HF-method in $[\text{Å}^3]$, $[\text{Å}^5]$, $[\text{Å}^7]$, $[\text{Å}^9]$.
SW D, SW Q, SW O, SW H   Multipole polarizabilities from the article by Stewart and Webster (SW) in $[\text{Å}^3]$, $[\text{Å}^5]$, $[\text{Å}^7]$, $[\text{Å}^9]$.

	TF D	TF Q	TF O	TF H	SW D	SW Q	SW O	SW H
He	1.86 (−1)	9.45 (−2)	1.13 (−1)	2.51 (−1)	1.95 (−2)	9.62 (−2)	1.16 (−1)	2.62 (−1)
Li^+	2.66 (−2)	4.60 (−3)	2.48 (−3)	1.47 (−3)	2.80 (−2)	4.64 (−3)	1.93 (−3)	1.50 (−3)
Be^{2+}	7.25 (−3)	6.21 (−4)	1.29 (−4)	4.97 (−5)	7.68 (−3)	6.33 (−3)	1.34 (−4)	5.41 (−5)
B^{3+}	2.72 (−3)	1.38 (−4)	1.65 (−5)	3.75 (−6)	2.89 (−3)	1.42 (−4)	1.79 (−5)	4.26 (−6)
C^{4+}	1.24 (−3)	4.23 (−5)	3.49 (−6)	5.32 (−7)	1.32 (−3)	4.29 (−5)	3.59 (−6)	5.62 (−7)
N^{5+}	6.43 (−4)	1.55 (−5)	9.15 (−7)	9.75 (−8)	6.87 (−4)	1.58 (−5)	9.41 (−7)	1.04 (−7)
O^{6+}	3.62 (−4)	6.66 (−6)	3.09 (−7)	2.82 (−8)	3.92 (−4)	6.74 (−6)	3.00 (−7)	2.47 (−8)
F^{7+}	2.23 (−4)	3.13 (−6)	1.09 (−7)	6.90 (−9)	2.39 (−4)	3.19 (−6)	1.10 (−7)	7.02 (−9)
Ne^{8+}	1.45 (−4)	1.64 (−6)	4.75 (−8)	2.70 (−9)	1.54 (−4)	1.64 (−6)	4.52 (−8)	2.30 (−9)

The electron densities used in the TFDW-HF-calculations are from reference [a] of Table 2. The numbers in round brackets (n) mean multiplication of the preceding number by 10^n.

Table 2. Multipole polarizabilities by the TFDW-HF-method:
1 Elements, references of Hartree-Fock-densities are marked by small letters and are given below.
2/3/4 TFDW-HF-dipole-, quadrupole, octopole polarizabilities in [Å^3], [Å^5], [Å^7].
5 Best available dipole polarizabilities from Teachout and Pack of from references below in [Å^3].
6 Best available quadrupole polarizabilities from references below in [Å^5].

1	2	3	4	5	6
Li [a]	12.9	58.4	453	21.7 CHF [k]	62.0 CHF [k]
Be^{+} [a]	1.4	2.0	5.4	2.53 CHF [k]	2.31 CHF [k]
B^{2+} [a]	0.36	0.26	0.34	0.66 CHF [k]	— —
C^{3+} [a]	0.13	0.06	0.04	0.246 CHF [k]	— —
Be [a]	4.8	13.5	65.5	6.93 BG	14.21 CHF [k]
B^{+} [a]	0.95	1.0	2.0	1.40 CHF [k]	1.17 CHF [k]
C^{2+} [a]	0.27	0.19	0.2	0.496 CHF [k]	0.217 CHF [k]
B [b]	2.6	3.6	23.1	2.85 [h]	5.55[o] CHF
C [b]	1.5	2.4	6.9	1.54 BG	2.28[o] CHF
N [b]	0.53	0.52	0.94	1.13 exp	1.06[o] CHF
O [b]	0.63	0.68	1.31	0.77 exp	0.675[o] CHF
F [b]	0.46	0.42	0.72	0.47 [h]	0.426[o] CHF
Ne [b]	0.36	0.30	0.49	0.395 exp	0.268 CHF [f]
Na^{+} [c]	0.14	0.06	0.04	0.140 CHF	0.0632 CHF [f]
Mg (HFS)	7.8	34.0	217	6.87 – 9.3 exp	23.1 C [n]
Al (HFS)	8.3	44.3	396	[11.0 SCF]	— —
Cl^{-} [c]	2.9	10.2	61	3.76 CHF	11.92 CHF [g]
Ar [c]	1.4	2.2	4.9	1.65 exp	1.957 CHF [g]
K [d]	23.5	241	2958	41.3 – 41.6 exp	211.5 ST [i]
K^{+} [c]	0.69	0.69	1.0	0.789 CHF	0.674 CHF [g]
Ca [d]	17.5	131	1288	19.0 – 21.1 exp	108.4 C [n]
Ca^{2+} [c]	0.43	0.33	0.37	0.475	0.29 CHF [g]
Sc [d]	13.8	90.2	753	[26.8 SCF]	— —
Ti [d]	10.9	71.4	564	[22.4 SCF]	— —
V [d]	9.6	57.5	423	[19.1 SCF]	— —
Cr [d]	8.84	47.8	344	[16.6 SCF]	— —
Mn [d]	8.5	38.2	255	[14.6 SCF]	— —
Fe [d]	6.9	32.8	209	[12.7 SCF]	— —
Co [d]	6.1	27.9	173	[11.3 SCF]	— —
Ni [d]	5.6	24.5	152	[10.2 SCF]	— —
Cu [d]	2.7	10.7	57.7	[9.1 SCF]	— —
Zn [d]	4.5	17.3	89.3	6.65 [l]	— —
Ga [d]	6.4	30.9	210	[9.31 SCF]	— —
Ga^{+} [d]	1.5	3.5	9.9	[3.01 SCF]	— —
Ge [d]	4.9	17.8	90.5	[6.97 SCF]	— —
Ge^{+} [d]	2.0	5.0	16	[3.11 SCF]	— —
As [d]	3.6	10.7	44.5	[5.2 SCF]	— —
As^{+} [d]	2.2	5.5	18.3	[2.73 SCF]	— —
Se [d]	3.2	8.8	32.4	[4.5 SCF]	— —
Se^{+} [d]	1.7	3.3	8.1	[2.32 SCF]	— —
Br [d]	2.5	5.9	18.5	[3.79 SCF]	— —
Br^{+} [d]	1.6	2.7	6.0	[2.13 SCF]	— —
Kr [d]	2.0	4.1	11.4	2.48 exp	3.26 [m]
Kr^{+} [d]	1.3	2.0	4.1	— —	— —
Rb (HFS)	22.1	283	3760	43.6 – 43.7	261.4 ST [i]
Ag^{+} [e]	0.75	1.02	1.9	— —	— —
Xe (HFS)	3.0	8.2	29.6	4.04 exp	5.31 [m]
Cs (HFS)	31.1	487	7580	52.6 – 52.9 exp	440.8 ST [i]
Ba (HFS)	26.2	302	3663	30.6 – 34.7 exp	312 C [n]

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The abbreviations mean:
HFS = Hartree-Fock-Slater
CHF = Coupled Hartree-Fock-approximation
SCF = self consistent field approximation (according to Teachout and Pack of lower quality)
ST = Sternheimer-approximation
BG = Bethe-Goldstone approximation (of high quality)
C = Coulomb approximation
exp = experimental.

energy part (20) with $\xi = 0.2$ for the rare gases. The results are given in Table 3, showing that $\xi = 0.2$ seems not to be a good approximation in the outer part of the atom. This is in agreement with Goodisman's suggestion that the complete kinetic energy term should be used outside a shell centred near the nucleus.

Table 3. Dipole-(D), quadrupole-(Q), and octupole-(O)-polarizabilities in [Å^{2L+1}] with $\xi = 0.2$. For comparison Doran's (s. Table 2) values by BG-perturbation theory are given.

	D	Q	O	D(BG)	Q(BG)	O(BG)
Ne	0.57	0.81	1.50	0.39	0.27	0.35
Ar	2.1	6.0	20.9	1.63	2.0	5.22
Kr	4.3	15.4	58.6	2.46	3.26	7.90
Xe	4.3	22.4	242	3.97	5.31	12.80

5. Conclusion and Discussion

By application of a statistical variation-perturbation method on spherical Hartree-Fock densities including a gradient correction to the kinetic energy, we got a large number of atomic and ionic multipole polarizabilities which were shown to be in good or reasonable agreement with the best available values in comparable cases. The TFDW-HF-method has the advantage of short computation times. It is not successful for negative ions and alkali like atoms and ions with their far reaching electron density from the "leucht-electron". In this case the semiempirical method with oscillator strengths, the Coulomb-[20] or the Sternheimer[21] method are more reliable.

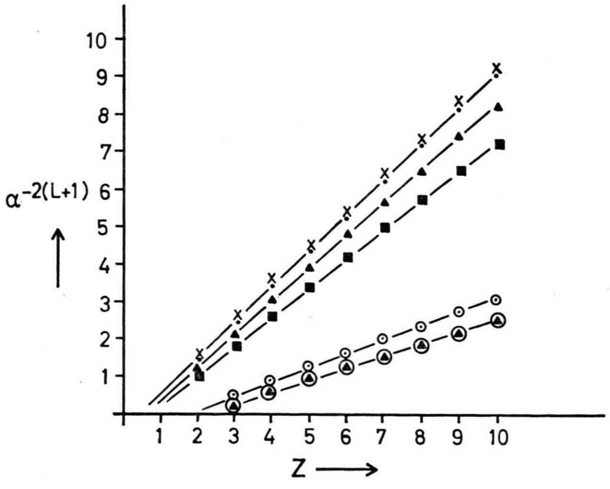

Fig. 1. Pauling plot for two-, three- and four electron systems. two electrons: ● dipole, × quadrupole, ▲ octopole, ■ hexadecapole; three electrons: ● dipole, ○ quadrupole (accidentally coincident to ⊙); four electrons: ▲ dipole, ○ quadrupole (accidentally coincident to (▲)).

The results for atoms and ions with $Z > 36$ are not so good which may depend on relativistic and correlation contribution to the atomic wave function. It is possible to take both corrections into account. Tomishima[22] constructed a relativistic statistical theory including the Weizsäcker correction. Gombás[23] and Schneider[24] discussed statistical expressions for the correlation. We did not use these modifications as in addition to the uncertain correction of the kinetic energy further energy corrections would obscure the results. The TFDW-HF-method serves as an easy semiempirical method for calculating reliable multipole polarizabilities.

Appendix

In his monograph Gombás[6] discussed in detail a simplified model for the calculation of electron densities and dipole polarizabilities for atoms and ions. For the polarizabilities he used

$$\alpha = \frac{K^2(r_0)}{2\int_0^{r_0} K(r)\,[\bar{\varrho}(r)]^{1/3}\, r\,\mathrm{d}r + (5\,\varkappa_k/6\,\pi\,e^2)\,K(r_0)} \tag{31}$$

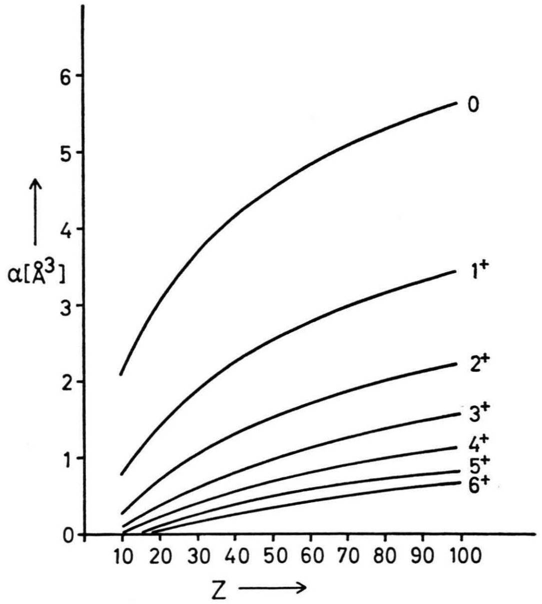

Fig. 2. Dipole polarizabilities in Gombás' model in [A^3] for ionization degrees from zero to six.

where

$$K(r) = \int_0^r [\bar{\varrho}(r')]^{1/3} r'^4 \, dr' , \quad \bar{\varrho}(r) \text{ electron density,} \tag{32}$$

r_0 boundary radius of the model.

As the old Gombás values for the rare gases isoelectronic series are often cited[1, 3], we give the complete results in Figure 2.

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