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DATA PAPER

A simple semiempirical model for the static polarizability of ions

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A concise analytical model for the static dipole polarizability of ionized atoms and molecules is created for the first time. As input, it requires, alongside the polarizability of neutral counterpart of a given ion, only the charge and elemental composition. This physically motivated semiempirical model is based on a number of established regularities in polarizability of charged monatomic and polyatomic compounds. In order to adjust it, the results of quantum chemistry calculations and gas-phase measurements available for a broad range of ionized multielectron species are employed. To counteract the appreciable bias in the literature data toward polarizability of monoatomic ions, for some molecular ions of general concern the results of the authors' own density functional theory calculations are additionally invoked. A total of 541 data points are used to optimize the model. It is demonstrated that the model we suggested has reasonable (given the substantial uncertainties of the reference data) accuracy in predicting the static isotropic polarizability of arbitrarily charged ions of any size and atomic composition. The resulting polarizability estimates are found to achieve a coefficient of determination of 0.93 for the assembled data set. The created analytic tool is universally applicable and might be advantageous for some applications where there is an urgent need for rapid low-cost evaluation of the static gas-phase polarizability of ionized atoms and molecules. This is especially relevant to constructing the complex models of nonequilibrium chemical kinetics aimed at precisely describing the observable refractive index (dielectric permittivity) of plasma flows. The data sets that support the findings of this study are openly available in Science Data Bank at https://doi.org/10.57760/sciencedb.07526.

Keywords: polarizability, ions, semiempirical model, quantum chemistry

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1. Introduction

The static electric dipole polarizability of a multielectron system as a property describing the lowest-order moment of induced response to an external electric field is known to be an essential fundamental quantity in many areas of atomic, molecular, optical, and chemical physics (basically, polarizability governs both electromagnetic field–matter interactions and interparticle collision phenomena).[1–7] However, accurate experimental and theoretical data for this pivotal electric property are widely available mainly for neutral atomic and molecular species.[6–15]

As for ions, the reliable literature values are predominately limited to singly and doubly charged monoatomic cations,[16–23] whereas both for highly charged atomic cations and especially for anions (both atomic and molecular) there is a lack of established data on polarizability. Indeed, the information available in the literature on the isotropic (scalar) polarizability values for multiply charged atomic species is essentially fragmentary,[16,21,22,24–26] and the polarizability estimates for negative monoatomic ions reported elsewhere can differ by tens of percent and even several times.[25–30] Simultaneously, very little is known about the polarizability of molecular ions and charged clusters, with a few exceptions for some singly charged diatomic,[31–42] small polyatomic,[43–45] and cluster ions.[46–50]

The noted knowledge gap on the polarizability of charged particles relates both to the difficulty of manipulating highly reactive and unstable species, such as ions, in an experiment[38,51–54] and to the fact that the precise evaluation of electric response properties of such electron-deficient and, even more so, electron-rich systems remains a hard nut to crack for conventional quantum chemical machinery.[21,25,28,29]

The accurate data on the polarizability of charged species are primarily of fundamental relevance to the interpretation of the respective spectra[18,29,53–56] and for the calculation of ion–molecular potentials.[57–59] At the same time, these data are also essential for several existing and emerging applications directly based on the intrinsic properties of ions themselves (quantum computing,[18,60,61] quantum metrology,[18,60,62] and development of optical frequency standards[18,21,23,53,60,63]) as well for a number of issues where an appreciable ionization of the gaseous medium, due to the specific physical properties of charged particles as compared with their neutral counterparts, critically affects the macroscopic characteristics (optical refractivity,[31,64–66] dielectric permittivity,[69–72] electrical conductivity,[73] molecular transport properties[44,45,74,75]) of ionized reacting gas or plasma.

In view of the foregoing, for miscellaneous areas of applications, mostly, when constructing the complex nonequilib-

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rium chemical kinetics models (involving a variety of charged species) aimed at precisely describing the observable refractive index (dielectric constant),[31,65–72] ion-induced chemical transformations,[58,76] and transport properties[44,74,75] of ionized reacting gas (plasma) flows, it would be highly desirable to have the simple theoretical tools that reasonably predict the effect of ionization on the polarizability of atoms, molecules, and clusters.

Such tools or, preferably, analytical models would also be helpful for the critical evaluation of known and at times conflicting experimental and theoretical data on the polarizability of charged species[16,26,38] and thus for making appropriate consensus recommendations. Specifically, notable uncertainty in the available theoretical data is relevant both for ions containing heavy atoms (the contributions from relativistic and spin–orbit effects, which are notoriously difficult to treat with routine electronic structure methods, increase with the nuclear charge Z)[13,18,19,25,28–30,77] and for negative ions in general, the description of the electric response of which is especially challenging for the theory due to the very diffuse character of the electron density distribution.[25,27–30,48]

Unfortunately, to our best knowledge, at the present state of the art in the field, there exist no models of this kind that predict the polarizability even for arbitrarily ionized atoms, let alone ionized molecules and clusters. However, it is fair to say that the main qualitative trends in polarizability of charged species are currently clear, at least for monoatomic ions. Particularly, the polarizability values for cations are generally smaller than those for neutrals, since the electrons in positive ions are more tightly bound by the field of the atomic core (in the cation, the positive charge of the nuclei is weaker shielded by electrons than in its neutral counterpart).[18] In contrast, negatively charged ions have increased polarizability, because their outermost electrons are very weakly bound.[29,78,79]

Another observed trend is that the polarizability of monoatomic species having a nuclear charge number Z and charge q is known to rapidly diminish within so-called isoelectronic sequences (number of electrons $N = Z - q$ for the members of a sequence is kept constant) as Z increases.[26,51,80–83] For instance, a set of essentially empirical expressions in terms of rather cumbersome rational functions of $q > 0$ has been proposed not long ago by Koch and Andrae[82,83] to describe this effect for individual isoelectronic series of atomic cations.

Finally, to complete the picture, it is worth noting that many years ago (at the turn of the 1980s)[16,81] approximate analytical dependences for the polarizability of an atomic ion with proton number Z and electron number N were obtained semiclassically within the framework of Thomas–Fermi (TF) model,[84,85] however according to the authors,[16,81] these formulas, due to their inherent limitations, apply only to multiply-charged atomic cations (i.e., at $N \ll Z$).

Thus, despite the existence of a number of established regularities, as far as we know, there have been no successful attempts to synthesize them into a universally applicable analytic expression for the polarizability of ionized species. In this regard, the primary objective of the present work is to fill this gap and develop a physically motivated (as much as possible) and practical analytic model that would enable evaluation — with a minimal amount of input data — of the static isotropic polarizability of ionized atoms and arbitrary-sized molecules in the gas phase with reasonable and uniform accuracy.

Because a model of this kind, due to the well-known impossibility of an analytical description of the multielectron systems from first principles, cannot help but contain some empiricism, for its adjustment of both accurate theoretical estimates and reliable measurements previously reported in the literature for a large range of charged multielectron species will be employed.

However, in view of the existing bias in the current body of evidence for the polarizability of charged particles toward monoatomic ions, in order to elaborate a more balanced model for polarizability of ionized multielectron compounds we will have to additionally invoke the results of our density functional theory (DFT) calculations. The latter will be carried out for a number of molecular ions of general relevance, whose electrical properties have not yet received considerable attention from researchers involved in electronic structure problems.

The remainder of this paper is organized as follows. In Section 2, a thorough description of the data acquisition methods is provided. In particular, Subsection 2.1 describes filling the ion polarizability database according to the available literature sources, and Subsection 2.2 contains details and results of our DFT polarizability calculations for molecular ions. In Section 3, we address the regularities in polarizability of ionized atoms and molecules and, accordingly, the model formulation. The results of model adjustment are then presented and discussed in Section 4. Section 5 contains a concise extract for researchers who are only interested in the practical use of our model or the ion polarizability data we assembled in their work. Finally, Section 6 summarizes our conclusions.

2. Assembling the data set for ionic polarizabilities

2.1. Analysis of the available literature

At the initial stage of research, in order to provide insight into the regularities in polarizability of charged species and adjust the semiempirical model to be created, we had to assemble a diverse, representative, and consistent data set of reliable polarizability values for ionized atoms, molecules, and clusters in the gas phase.

We note, incidentally, that since the electronic polarizability values for ions calculated by various theoretical approaches are known to depend markedly on the level of treatment chosen,[17,22,25–30] it is worthwhile to think of the change in the static dipole polarizability due to ionization in relative terms, i.e., as the ratio of the polarizability of an ion α_i to the polarizability of its neutral counterpart α_n expressed as $\xi = \alpha_i/\alpha_n$. In doing so, the errors in the reported α_i and α_n magnitudes inevitably intrinsic to any electronic structure calculations are supposed to, at least partially, counteract each other.

To begin with, all the data we found for various charged atoms (ranging from H up to Ba as well as for several heavier elements including Pt, Au, Hg, Tl, Pb, At, Fr, Fr, and Ra) were involved for this purpose, namely, the results of multiple theoretical calculations[16,17,19,21–30,44,51,59,82,86,87] and measurements[16,53] together with some expert estimates reported in related compendia.[73,75]

Then, we introduced into the fit data set the theoretical[32–37,39–44] and experimental[38] data obtained elsewhere for di- (H_2^+, HeH^+, Li_2^-, Li_2^+, NeH^+, CH^+, CO^+, OH^-, CF^+, F_2^-, and F_2^+), tri- (HCO^+, N_2H^+, and CF_2^-), and small polyatomic (CF_2^+, CF_3^-, CF_3^+) ions. Next, the potentially not very accurate polarizability estimates for N_2^+ and O_2^+ cations adopted in reference[31] were used. Finally, we brought into play the calculated polarizability values for several boron-, carbon-, aluminum-, and palladium-containing atomic cluster ions.[46–50]

The meaningful data extracted for our purposes from the above-cited studies, *viz.*, the polarizabilities of an ion α_i and of its neutral counterpart α_n, are summarized in Table S1 of supplementary material. If the aforementioned papers on ions did not list the necessary α_n values, we borrowed the missing neutral polarizabilities from elsewhere.[8,11–13,45,88]

Altogether, our compiled data set includes the literature-based ξ values for 203 monoatomic and 47 molecular and cluster ions, with the total number of data points surpassing 460 (for many charged particles, different data points can refer to the same ion). As the numbers here indicate, monoatomic ions are better represented in this body of data than polyatomic ones, therefore, for completeness it would be desirable to supplement further the collected data with ξ values for extra molecular ions.

In effect, the data gathered in this table vary greatly in origin and in potential accuracy, and hence it is hardly possible to expect the internal consistency of the elaborated data set even if one considers the ξ values for the same charged systems.

Indeed, even for such "textbook" system as H^-, the discrepancy among the calculated polarizability values obtained within the framework of modern high-precision electronic structure methods can exceed 10%.[25,28] At the same time, for some other negative atomic ions, the magnitude of the spread among different theoretical estimates can be even more discouraging (in particular, for C^-, Al^-, K^-, Cs^-, Pt^-, and Au^- it can reach several times[28–30,44,51,59,75,82]).

For positive monoatomic ions (such as C^{2+}, C^{3+}, Na^+, Al^+, Si^{4+}, Ar^{3+}, Rb^+, and Tl^+), the inconsistency in data from different sources can also be quite significant.[16,19,21–26,44,59,73,75,82,86] For example, for Tl^+, the α_i values calculated within the time-dependent (TD) DFT[59] and restricted Hartree–Fock (RHF)[82] frameworks differ by more than a factor of two.

Thereby, in order to properly quantify the trends in polarizability of charged species and, afterward, to reasonably adjust the model to be elaborated, it makes sense to assign to the categories of data points obtained using certain techniques the relative weights that would characterize somehow the validity of the data involved.

The corresponding weights w_i we adopted for each data point are also included in the tables of supplementary material. As can be seen there, the results of very recent precision relativistic coupled-cluster calculations for several atomic ions reported in references[25,28] were weighted ten times more than the somewhat obsolete results of single-reference self-consistent field (SCF)[33] and configuration interaction (CI)[32] calculations or the estimates of obscure quality[31] for some molecular ions (Li_2^+, Li_2^-, CH^+, N_2^+, and O_2^+).

Accordingly, the credibility of the data from other sources was voluntaristically ranked on the scale from 1 to 10. For instance, both the α_i values recommended in references[16,73] on the basis of the critical review of experimental data and the ionic polarizabilities calculated by using the fourth-order perturbation theory method[27,34,43] were weighted by a factor of 6, whereas the non-relativistic TD-DFT based values for monoatomic ions by Gould and Bučko[59] were taken into account with smaller weights ranging from 5 (for the lightest atoms up to Ar) to 3 (for atoms from Ag).

2.2. DFT calculations of this work

It is regrettably true that despite the impressive amount of data on the polarizability of charged species now available, many molecular ions of interest to combustion, atmospheric, electric discharge, and shock-induced plasma chemistry as well as to astrochemistry were not mentioned above in Subsection 2.1 due to the lack of information necessary to determine the α_i/α_n ratio. Hence, in order to elaborate a more universal model for describing the effect of ionization on the static polarizability of multielectron systems, which would be more focused on the polarizability of molecular ions rather than monoatomic ones, we had to augment the data collection for polarizabilities of ionized species with the results of authors' own DFT calculations.

Notice that the choice of DFT framework as a workhorse for static polarizability calculations in this work is due to the remarkable efficiency of this computationally inexpensive methodology in calculating the electric properties of multielectron systems compared with a number of more computation-intensive techniques.[7,9,12,89–96]

2.2.1. Selection of the appropriate computational model

In order to choose the most suitable DFT functional that should be applied to calculate the relative polarizability of molecular ions ξ, we benchmarked the performance of a number of popular hybrid functionals against the reference ξ values for those ions from the literature-based data set described in Subsection 2.1 for which the known polarizability data are the most reliable.

Thus, the reference (benchmark) data set included the ξ data of different origin (Refs. [8,11–13,16,17,19,21,22,25–29,32–42,44,48,51,59,73,82,86–88]) for the monoatomic ions of first- and second-row elements of the periodic chart as well as for some diatomic (H_2^+, Li_2^-, Li_2^+, HeH^+, NeH^+, CH^+, CO^+, OH^-, F_2^-, F_2^+, CF^+) and small polyatomic ions (CF_2^-, CF_2^+, CF_3^-, CF_3^+, C_3^-, C_4^-, C_5^- C_6^-). The list of data points included in the benchmark data set of 94 charged species is indicated in Table S1 of supplementary material. In order to resolve the data inconsistencies (if any), the definite reference ξ values were determined by averaging the ξ data from various sources available for the same ion according to weights w_i assigned to particular data points in Subsection 2.1.

The preferred functional for DFT calculations was selected among the following set of popular hybrid alternatives: BH&HLYP,[97] B3PW91,[98] B3P86,[99,100] B3LYP,[100] B1B95,[101] mPW1PW91,[102] mPW1LYP,[102] mPW1PBE,[102] mPW3PBE,[102] PBEh1PBE,[103] B98,[104] B97-1,[105] B97-2,[106] PBE0 (PBE1PBE),[107] BMK,[108] X3LYP,[109] and M06.[110]

Following references,[9,11,12,89,90,111,112] the Dunning's correlation-consistent triple-zeta basis set with diffuse functions aug-cc-pVTZ[113] was used both for the benchmarking and for subsequent polarizability calculations. To find the electronic isotropic polarizability (1/3 of the trace of polarizability tensor) of the ions and neutrals in question, the method by Cammi *et al.*[114] was applied to their equilibrium structures. This implies that the analytical derivatives of the energy with respect to field strength were computed within the coupled-perturbed Kohn–Sham (CPKS) formalism.[115] The required quantum chemical calculations were carried out throughout this work with the Firefly QC program package[116] partially based on the GAMESS(US) source code.[117]

Besides testing DFT methods themselves, we were also interested in analyzing the performance in reproducing ion polarizability of the techniques based on the second-order perturbation treatment of electron correlation, such as MP2,[118] B2PLYP,[119] and mPW2PLYP,[120] because these methods are considered as the standard reference points for assessing the accuracy of polarizability calculations.[9,25,90,93,121]

The aggregated results of these tests, namely, the mean logarithmic error (MLE) determined as $\varepsilon_{\mathrm{MLE}} = \sum_i |\lg(\xi_i^{\mathrm{calc}}) - \lg(\xi_i^{\mathrm{ref}})| / \sum_i 1$ and the maximum logarithmic error (MaxLE) as provided by $\varepsilon_{\mathrm{MaxLE}} = \max_i |\lg(\xi_i^{\mathrm{calc}}) - \lg(\xi_i^{\mathrm{ref}})|$ for the calculated ξ^{calc} and reference ξ^{ref} data vectors are presented in Fig. 1. Note in this connection that the decimal logarithm of the quantity of interest is taken here because ξ can vary drastically.

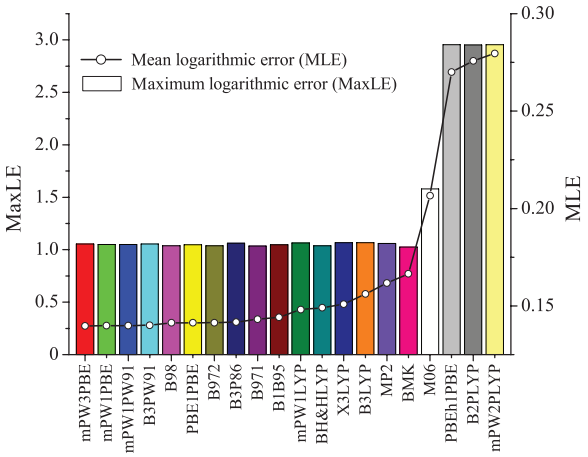


Fig. 1. The mean and maximum errors in the logarithmized values of relative polarizability of ions ξ obtained by using different methods with aug-cc-pVTZ basis set (the data bars are arranged in order of increasing MLE).

As seen here, most of the considered functionals, except for some individual outliers such as BMK, M06, and PBEh1PBE, describe the change in polarizability during ionization quite well, at least better than the "standard reference" MP2 method.

Interestingly enough, the double-hybrid density functionals B2PLYP and mPW2PLYP, which are originally designed to reproduce the energies of neutral ground-state systems,[119,120] but are also regarded as suitable for calculating the electrical properties of neutral molecules,[9,30,95,122,123] yield the largest mean and maximum deviations from the reference polarizability values in our case. According to our calculations, the overall worst performance of these DFT methods with perturbative second-order correlation over the benchmark data set is mainly due to the large errors obtained for multiply-charged monoatomic ions such as Ne^{8+} and F^{7+}.

With that, the best performance (if measured by MLE) is delivered by the 1998 modifications of the Perdew–Wang hybrid functional[124] proposed by Adamo and Barone[102] (*viz.*, PW3PBE, mPW1PBE, and mPW1PW91), however it must be admitted that the superiority of these top-three (in terms of

MLE) performers over a number of other fairly old DFT models, such as B3PW91, PBE1PBE, B98, B3P86, or the functionals of the B97-*n* family, is essentially nominal due to vanishingly small advantage in MLE and MaxLE metrics. Formally, the best DFT results were obtained with the mPW3PBE functional developed by Adamo and Barone.[102]

By and large, these results were quite expected given that at the time these quite old DFT functionals were created (until the early 2000s), the ability to give reasonable electron densities, as a rule, was not implicitly sacrificed for the accurate thermochemistry calculations, as has often been the case in developing more recent DFT formulations (see some references[93,96,125–133] for the related lively discussion initiated in 2017 by Medvedev *et al.*[125]), whereas it is a correct description of electron density that is necessary for accurate prediction of electric-field response properties.[93,96,133]

Incidentally, the aforementioned seminal paper of Medvedev *et al.*[125] focused on the analysis of electron density distribution in isolated atoms and, more significantly in the present context, monoatomic cations, the DFT functional providing the best densities turned out to be the one that, according to our benchmark calculations, yields the most accurate relative polarizabilities of ions ξ (mPW3PBE). This curious fact suggests that the metric Medvedev *et al.*[125] used to assess the quality of the density distribution has something to do with the relative polarizability of ions.

In view of the above and also because the mPW3PBE functional, according to some earlier studies,[131,132,134] reproduce rather well the electric properties of neutral molecules, we decided to use this version of DFT in further ion polarizability calculations. Meanwhile, we cannot fail to admit that the mPW3PBE functional is in fact rarely used to describe the dipole moment and polarizability of molecules and clusters.

Lastly, we note that although the performance of various computational methods in relation to the polarizability of neutral species has been studied very intensively in recent years,[9,89–91,96,121–123,131,132] the authors are not aware of any exhaustive benchmark studies of various DFT implementations for calculating ion polarizabilities. Therefore, we believe that this part of our study has independent value beyond the utilitarian brute-force search for an optimal DFT procedure, and the data for ξ we collected, in light of the discussion began with the Medvedev *et al.*'s article,[125] can be used for new rigorous tests of DFT developments in the future.

2.2.2. New results for molecular ions

Thus, to complement the literature-based data set described in Subsection 2.1, the DFT calculations of polarizability at the mPW3PBE/aug-cc-pVTZ level of theory were performed in the present work for extra 72 charged molecules that are abundant in the combustion products,[135–137] shock-heated air,[138,139] discharge plasma,[140–144] Earth's ionosphere,[145,146] and, at last, astrophysical environments.[147] These ions range in size from diatomics to $C_6H_7^+$ cation, containing 13 atoms.

Besides, for CO^+, O_2^+, HCO^+, and N_2H^+ cations of importance to plasma and interstellar matter chemistry[135,138,147] we carried out additional DFT calculations, the results of which, in a sense, duplicate the literature data for these species[31,41,43] included in the data set in Subsection 2.1.

A comparison of the ξ values we obtained for CO^+, HCO^+, and N_2H^+ cations with those provided employing highly correlated *ab initio* methods[41,43] further supports our choice of computational model (absolute error in ξ for these ions is within 0.1), while for dioxygen cation we found a quarter lower relative polarizability than that adopted in reference.[31]

By the way, once the equilibrium structures of the molecular ions under study have been determined, it was not difficult to simultaneously derive the corresponding values of the permanent dipole moment μ_D (if present) — another basic electric property of multielectron compounds, along with polarizability, entering the expressions for interparticle potentials and optical density (dielectric permittivity) of gaseous media.[5–7] Although this work focuses specifically on the ion polarizability, the dipole moment data obtained along the way at the mPW3PBE/aug-cc-pVTZ computational level (as the expectation value of the corresponding operator) will also be useful wherever polarizabilities of ions are required.

Meanwhile, the dipole moment values we obtained for a number of molecular cations (NH^+, OH^+, CO^+, HCO^+, and N_2H^+) were in good consistency with the data calculated previously by using the fourth-order perturbation theory[43] and coupled-cluster approach[41,62] (the maximum absolute and mean unsigned errors for this small sample of reference data[41,43,62] are 0.3 and 0.2 D, respectively).

Eventually, the found α_n, α_i, and ξ values together with the μ_D magnitudes determined incidentally were summarized in the Table S2 of supplementary material. In this connection, we note that to all the ξ values obtained in our CPKS DFT calculations, the same relative credibility weights w_i have been assigned as we put in Subsection 2.1 for most other DFT-based data, i.e., equal to 5.

3. Established regularities and model elaboration

As stated above in Section 1, the isotropic polarizabilities of anions are typically larger than those of neutrals, whereas the positive ions have a reduced polarizability compared with their neutral counterparts. This tendency is well illustrated in Fig. 2, where the actual ξ values from the data collection outlined in Section 2 are plotted against N/Z. We note, in passing, that the latter dimensionless quantity, sometimes called

the ionization degree, is commonly used as a natural variable to describe ionized states of atoms and molecules within statistical models[16,81,84,148,149] and DFT.[150]

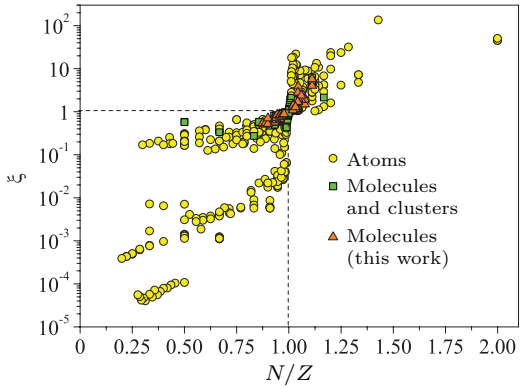


Fig. 2. The relative polarizability ξ of ionized atoms, molecules, and clusters as extracted from Refs. [8,11–13,16,17,19,21–51,53,59,73,75,82,86–88] and DFT calculations of this work versus N/Z (N and Z are the electron and proton numbers).

It is remarkable that the relative polarizability of atoms under strong ionization, i.e., with a significant deviation of the N/Z ratio from unity, can vary over orders of magnitude. As seen, the $\xi(N/Z)$ dependence for atomic ions is not straightforward but seems to be close to a power or exponential law. At the same time, the available data on molecules and clusters, as we observe in the graph in Fig. 2, do not allow us to trace the effect of change in the charge of a system in as wide a range of the ionization degree as can be done for atoms, however it can still be concluded that the magnitude of the effect for monoatomic and polyatomic species is about the same (for identical N/Z values).

To quantify the outlined tendency of ξ growth with the increase of N/Z, let us try to invoke the asymptotic expressions for the polarizability of multiply-charged monoatomic cations[16,81,148] analytically obtained within the semiclassical framework of Thomas–Fermi model.[84,85] It is easy to deduce from these findings that in the limit of strong ionization (when the intra-atomic potential is close to the unscreened Coulomb field of the nucleus[16,148]) the ratio of the polarizability of a strongly positively charged atom ($N \ll Z$) to the polarizability of its neutral counterpart ($N = Z$) is governed simply by

$$\xi(N \ll Z) = \left(\frac{N}{Z}\right)^3. \tag{1}$$

According to this expression, the relative polarizability of a multiply charged cation must fall monotonically with each detached electron, i.e., with a decrease of the N/Z ratio.

In this regard, (i) it would be worthwhile to quantify the actual relevance of Eq. (1) to multiply-charged atomic cations and (ii), considering the fact that Eq. (1) as it is at least qualitatively correctly describes the anticipated $\xi(N,Z)$ dependence at any ionization degree, it is interesting to look at extending its applicability to moderately charged atomic cations and (possibly) to anions.

Accordingly, let us compare now the semiclassical $\xi(N,Z)$ dependence provided analytically by Eq. (1) with the ξ data for real monoatomic ions. For this purpose, it is also convenient to use the ionization degree N/Z as an independent variable for a uniform representation of a variety of the ξ data on different ions. A relative increase (decrease) in the static polarizability upon ionization estimated by Eq. (1) is shown against N/Z in Fig. 3 as compared with the ξ values from the assembled data set for some monoatomic ions of some first- and second-row elements (B, C, N, O, Ne, Si, S, and Ar)[16,17,22,24,26,44,51,59,73,75,82,86,87] for which the ξ values are known in the broadest range of ionization degree (see Subsection 2.1). Note also that if there are different ξ values for the same ion in the data set, the weighted arithmetic means of relative polarizabilities we found in the literature (based on the weights assigned to these data points in Section 2) were used in the plotting of Fig. 3.

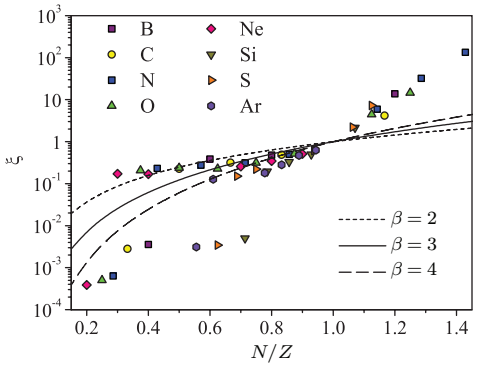


Fig. 3. The relative polarizability ξ of an ionized atom versus N/Z according to the semiclassically derived Eq. (1) (solid curve) and its analogue — Eq. (2) — with a modified power exponent (dot for $\beta = 2$ and dash for $\beta = 4$) together with the actual ξ values for various atomic ions based on the data reported elsewhere[16,17,22,24,26,44,51,59,73,75,82,86,87] (symbols).

As seen here, expression (1) describes the polarizability of multiply-charged atomic cations, contrary to our expectations, only semi-quantitatively. In point of fact, the actual $\xi(N/Z < 1)$ dependence is not universal, but differs greatly from element to element, especially at $N/Z < 0.8$. In the latter case, the curve given by Eq. (1) virtually lies somewhere between the literature ξ data points.

In effect, Eq. (1) works well only for slightly charged cations ($0.8 < N/Z < 1.0$), whereas for anions in question, it seems to seriously underestimate the observed increase in polarizability with electron attachment. Nevertheless, we must admit that equation (1) generally follows the observed trend of increasing polarizability with the N/Z ratio. Therefore, it would be tempting to modify Eq. (1) in some way so that it better corresponds to the data for real multielectron systems (arbitrarily charged atoms and, more importantly, charged molecules and clusters).

The first thing that comes to mind in this context is to stay within the physically reasonable power function of the

natural variable N/Z and somehow adjust the exponent in expression (1). This intention provides a basis for generalization of Eq. (1) to any atomic or even polyatomic species. Indeed, the ratio of α_i to α_n can be stated for an arbitrarily charged multielectron component in the form

$$\xi(N,Z) = \left(\frac{N}{Z}\right)^{\beta}, \tag{2}$$

where the power exponent β (equal to 3 within the semiclassical framework[16,81,148]) is thought as the fitting variable of the model.

Clearly, if we vary this exponent, say, from 2 to 4, the resulting $\xi(N/Z)$ behavior can be noticeably affected. However, as evident from Fig. 3 where the respective $\xi(N/Z)$ curves are additionally provided, in order to describe the observables, it is not enough to set the exponent β to a certain constant of the order of unity. In contrast, it seems that the exponent β in Eq. (2) is to be represented as a complicated function of at least N and Z numbers and, perhaps, some other properties of the system. This fact is illustrated in Fig. 4, where the β_{obs} values that correspond to the data points plotted in Fig. 3, granted Eq. (2) is used to describe them, are shown against N/Z. To guide the eye in Fig. 4, the data points referring to the same element are connected by lines, and the β_{TF} value according to the TF theory-based analysis[16,81,148] is also marked by a horizontal segment at near-zero N/Z.

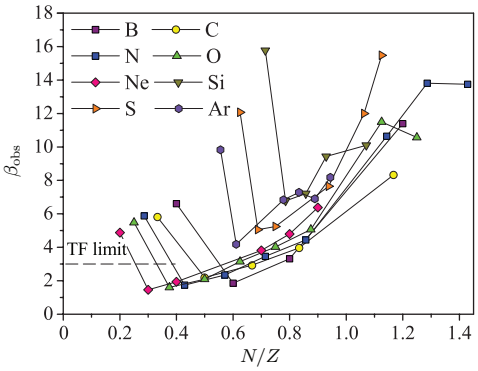


Fig. 4. The observed $\beta_{obs} = \ln(\xi)/\ln\left(\frac{N}{Z}\right)$ values for the atomic ions presented in Fig. 3 against N/Z.

Alas, by analyzing the data depicted in Figs. 3 and 4, it must be stated that the exact nature of the β function that could describe, within Eq. (2), the influence of electron attachment and detachment on the gas-phase static dipole polarizability of arbitrary atoms and molecules is, at first glance, not self-evident even for the monoatomic ions of first- and second-row elements. Nevertheless, let us try to scrupulously analyze the entire data collection and construct a proper analytical expression for β.

So, we plainly see from the plots displayed in Fig. 4 that the β_{obs} values corresponding to the observed change in polarizability of atoms of first- and second-row elements with ionization and electron attachment are indeed not equal to 3, as is implied by TF model,[84,85] even in the limit $N/Z \to 0$. In fact, the β_{obs} values of highly ionized monoatomic cations, at least for the elements considered in Figs. 3 and 4, are markedly greater than 4. Then, as the ionization degree increases, there is a noticeable drop in the observed β values down to about 2–3, which is then replaced by a monotonic increase up to the order of 10 reached for anions.

Thus, the $\beta(N/Z)$ function, though not monotonically, generally grows with N/Z, but an important local feature of the observed $\beta(N/Z)$ behavior was not captured in the analysis conducted for the ions of light atoms provided above. As can be deduced from Fig. 5, where the β_{obs} values for the ions — without loss of generality of the discussion — of the group 1 (alkali) atoms based on the α_i data reported elsewhere[16,19,24–26,28,59,73,82,86,87] are plotted as a function of N/Z (again, in the presence of different α_i values for the same ion, weighted averaging was applied), the observed $\beta(N/Z)$ function appears to have a pole at $N/Z = 1$. Indeed, for ions of heavy atoms, for which the N/Z argument is only slightly different from unity, there is a sharp increase in the apparent value of β function, and this $\beta(N/Z)$ behavior can be described as an inverse power of $|1 - N/Z|$ (see Fig. 5, where this fit is additionally sketched for the alkaline monoatomic ions under consideration).

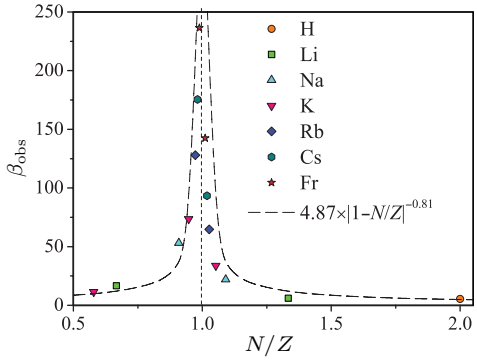


Fig. 5. The observed $\beta_{obs} = \ln(\xi)/\ln\left(\frac{N}{Z}\right)$ values for the atomic ions of the group 1 elements based on references[16,19,24–26,28,59,73,82,86,87] against N/Z (symbols, the vertical dotted asymptote is a guide to the eye) together with the best fit to these data obtained using the inverse-power function of $|1 - N/Z|$ (dashed curve).

It is also clear that such a feature of the $\beta(N/Z)$ function could not be readily observed for the ions of the lightest atoms considered in Fig. 4, since even for the singly charged atomic ions of first- and second-row elements, the value of N/Z ratio does not approach to unity to closer than 0.05. Interestingly enough, the molecular and cluster ions containing heavy-element nuclei, as can be seen from the analysis of relevant data provided in the supplementary material, follow the same trend.

Regrettably, we cannot rationalize the existence of the pole of the $\beta(N/Z)$ function when describing the polarizabil-

ity of ions by Eq. (2), and thus we will treat this feature simply as an empirically established trend.

Note further that according to the semiclassical analysis within the TF framework,[84,85] the polarizability of monoatomic cations should additionally depend on the parity of electron number in a given compound N, *viz.*, along isoelectronic sequences, the polarizability of open-shell positive ions (with an odd number of electrons) is expected to decrease with Z weaker than the polarizability of closed-shell cations (with an even number of electrons).[16,81,148] However, it is difficult to validate this prediction against the available and essentially limited data set that does not comprise enough ξ data for atomic and, *a fortiori*, molecular cations over a wide range of ionization degree. Nevertheless, inasmuch as the parity of N is known to significantly affect various physical properties (including polarizability) not only of atoms, but also of polyatomic structures,[50,94,151–153] the influence of this factor should also be taken into account when constructing the model applicable to charged particles of any size.

At last, the β function, which governs the N/Z dependence of the α_i/α_n ratio, along with its dependence on the ionization degree and number of electrons, should also be determined by the elemental composition of ion. Indeed, a very basic observation is that the isotropic polarizability of a multielectron system generally increases as the number of constituting electrons N,[94,154,155] which in the case of neutral particle coincides with the number of protons Z (in other words, isotropic electronic polarizability is roughly additive for subsystems[156,157]).

At the same time, we know that polarizabilities of atoms decrease as one moves from left to right in a fixed row of the periodic table,[13,111] i.e., with an increase in the number of outer (valence) electrons N_{out}.[84] In fact, there is an inverse power-function relationship between α_n and N_{out} in a given row, with the magnitude of the corresponding exponent ranging significantly (from 3 to 9).[13]

However, for more accurate analytical representation of this "horizontal" trend, following Cambi *et al.*,[158] the effective number of outer-shell electrons N_{out}^{eff} is to be used instead of N_{out} to account for the additional influence of the inner-shell (core) electrons, the number of which we denote as N_{inn} (see also reference[15] for related discussion). In doing so, for the elements starting with Li, the N_{out}^{eff} values can be calculated as follows:

$$N_{out}^{eff} = N_{out}\left[1+\left(1-\frac{N_{out}}{N_{inn}}\right)\left(\frac{N_{inn}}{N_{out}}\right)^2\right]. \tag{3}$$

In particular, according to this expression, for Li ($N_{out}=1$), N ($N_{out}=5$), Ne ($N_{out}=8$), Mg ($N_{out}=2$), S ($N_{out}=6$), Ar ($N_{out}=8$) atoms, the effective number of outer electrons N_{out}^{eff} takes the values 1.22, 4.39, 7.04, 3.11, 6.94, 8.49, respectively. Clearly, for H and He, $N_{out}=N_{inn}=N_{out}^{eff}$, and no correction for the core electrons is required.

Because isotropic polarizability, as mentioned above, is to a good extent an additive quantity, the outlined "horizontal" regularity for atoms can be generalized to particles of an arbitrary size, and the sum of the effective numbers of outer electrons N_{out}^{eff} of atoms that make up the polyatomic compound $S_{out}^{eff}=\sum N_{out}^{eff}$ is to be taken as an argument of the inverse power-function for α_n in the latter case.

In this way, the neutral polarizability α_n of an arbitrary compound, given the observed dependence on the numbers of protons (electrons) and valence electrons, scales as $\sim Z^p/(S_{out}^{eff})^q$, where the p and q exponents are of the order of unity, and for the data set we assembled in Subsection 2.1 (containing the relative polarizabilities of both atomic and molecular ions), $p\approx 1.4$ and $q\approx 1.16$. Note also that this scaling law in relation to the polarizability of neutral atoms is nothing but a formal representation of the well-known periodic pattern.[13,159–163]

Accordingly, it is also reasonable to expect a similar scaling behavior for the polarizability of ions α_i (of course, in this case, the power exponent values responsible for the dependence on Z and S_{out}^{eff} arguments will be somehow different). Therefore, in the sought-for expression for the β function that specifies the N/Z dependence of the α_i/α_n ratio, it is sensible to introduce the power-law Z and S_{out}^{eff} dependences as well.

In view of the above intentions, we were looking for such a not too burdensome function for β that, when substituted in Eq. (2), best reproduce the relative polarizability ξ for the assembled set of ions. After a series of preliminary trials and close examination of the collected data, the numerical experiments with various elementary functions have resulted in the following 10-parameter expression for the β exponent given by

$$\beta = \frac{p_0\exp\left[p_1\frac{N}{Z}+p_2\sqrt{\frac{Z}{N}}(N \bmod 2)\right]}{\left|1-\frac{N}{Z}\right|^{p_3}\left[1+p_4\exp[-p_5(\frac{N}{Z}+p_6\ln\frac{Z}{S_{out}^{eff}}+p_7)^2]\right]} \times\frac{Z^{p_8}}{\left(S_{out}^{eff}\right)^{p_9}}, \tag{4}$$

where $p_0,\ldots,p_9$ are dimensionless fitting parameters, N and Z are the total numbers of electrons and protons in a given charged compound (note that the modulo-2 division is used here to check N for parity), and S_{out}^{eff} is the sum of the effective numbers of outer electrons [in turn, determined according to Eq. (3)] over the atoms constituting the neutral counterpart of an ion at issue ($S_{out}^{eff}=\sum N_{out}^{eff}$).

As we see here, the structure of this expression, although somewhat overloaded with adjustable parameters, includes as arguments only a few basic dimensionless (integer) quantities such as the numbers of protons, all-electrons, valence electrons as well as their ratios.

The first factor on the right-hand side of Eq. (4) represents the $\beta(N,Z)$ dependence. In particular, its numerator describes both a general trend of β increase with a degree of ionization N/Z and the influence of parity of N. The denominator in turn is responsible both for the presence of the pole of this function at $N/Z = 1$ evinced by Fig. 5 and for the nonmonotonicity of $\beta(N/Z)$ function visualized in Fig. 4.

The second factor in Eq. (4) stands for the discussed above dependence of β on the elemental composition of ion, expressed *via* power functions of Z and $S_{\text{out}}^{\text{eff}}$. Meanwhile, a certain dependence on these quantities also presents in the denominator of the first factor of Eq. (4) that describes the nonmonotonicity of $\beta(N/Z)$ function displayed in Fig. 4. Here, when constructing Eq. (4), we actually took into account the relationship we have empirically found between the position of the $\beta(N/Z)$ function minimum and the $Z/S_{\text{out}}^{\text{eff}}$ ratio.

Thus, our model for β, consisting basically of Eqs. (2) and (4), requires as input data, apart from the Z and N numbers, only the elemental composition of the ion (in order to calculate the sum of the effective numbers of the outer electrons of the constituting neutral atoms). The particular values of $p_0,\ldots,p_9$ parameters can be found by fitting the model to the assembled data set described in Section 2.

It should also be underlined that, when developing a model for evaluating the effect of ionization on the polarizability of atoms and molecules, we tried to offer the simplest possible analytical expression, the use of which would not require knowledge of the intrinsic nature of the electronic structure of the considered electron-deficient and electron-rich systems.

In addition, we would like to avoid integrating into the expression for β such apparently relevant quantities as the ionization energy and electron affinity of neutral species, not to mention any additional related properties such as the successive ionization potentials and electron affinities, because their accurate determination requires essentially no less computational effort than the calculation of ion polarizability itself.

It may well be that the known ξ data could be slightly better fitted if we further complicate the composite function provided by Eq. (4) substituted into Eq. (2) through increasing the number of freely adjustable parameters or by introducing extra meaningful properties of ions and neutrals as new arguments in Eq. (4). However, despite our best effort, we were unable to find other more or less physically relevant functional forms that, with a similar number of fitting parameters, would markedly improve the accuracy of the fit compared to Eq. (2) coupled with Eq. (4).

4. The model adjustment and related discussion

In order to arrive at the $p_0,\ldots,p_9$ fitting parameters values [appearing in Eq. (4) for the effective variable β] that ensure the best model performance across the range of possible ξ variation, the diverse and extensive fit data set was compiled as described in Section 2. It covers, aside from 465 literature data points for 250 individual charged species (with q changing from -3 to 26) based principally on theoretical and expert estimates reported previously[16,17,19,21–37,39–44,46–51,59,73,75,82,86,87] as well on the credible measurements,[16,38,53] the results for 76 extra molecular ions of general concern (mostly singly charged anions and cations) obtained in our CPKS polarizability calculations within the mPW3PBE/aug-cc-pVTZ model chemistry. The full list of data points employed for model optimization (overall, 541 items) is accessible as supplementary material.

Note that according to a known rule-of-thumb,[77,157] the size of the resulting data set is more than sufficient to reliably determine the ten fitting parameters entering the expression for β. In effect, with so many data points, it would be acceptable to increase the number of free parameters of the model up to $\sqrt{541} \approx 23$, but as mentioned in Section 3 above, we do not think it is appropriate.

As previously discussed in Section 2, in order to properly configure the model we put forward, it is worth taking into account the potential reliability of the gathered data, characterized by the corresponding weights w_i attributed to each data point and, accordingly, indicated in the tables of supplementary material. So long as the approximated quantity ξ can vary by a few orders of magnitude (see Fig. 2), the model was fitted to the base-10 logarithmized reference values of relative polarizabilities. With this in mind, the weighted root-mean-square deviation (WRMSD) error for logarithmized ξ as provided by $\varepsilon_{\text{WRMSD}} = (\sum_i w_i[\lg(\xi_i^{\text{calc}}) - \lg(\xi_i^{\text{ref}})]^2/\sum_i w_i)^{0.5}$ was adopted as metrics for evaluating the fitting quality.

In Table 1 are given the final values of fitting parameters providing the best match of the predictions by means of the model consisting essentially of Eqs. (2) and (4) to the reference ξ data from the tables of supplementary material. The information presented here suggests that all the parameters have non-extreme magnitudes actually matching the trends identified in Section 3 above.

It is also noteworthy that this optimized set of $p_0,\ldots,p_9$ parameters, when inserted into Eq. (4), yields for the β function in the strong ionization limit $N/Z \to 0$ significantly higher values (determined mainly by the magnitude of p_0) than is the case with the TF theory-based analysis[16,81,148] (remember that $\beta_{\text{TF}} = 3$).

Table 1. The optimized set of fitting parameters.

p_0	p_1	p_2	p_3	p_4	p_5	p_6	p_7	p_8	p_9
6.141	0.074	–0.494	0.464	3.030	15.722	–1.005	–0.257	0.420	0.605

Now that we have configured the proposed model, let us assess the correlation between its outputs and the known values of relative polarizability. A graphical illustration of the model performance is provided by Fig. 6, where for all charged species present in the data set (described in Section 2) the ξ values delivered by Eq. (2) in conjunction with Eq. (4) using the optimized $p_0, \ldots, p_9$ values are shown versus the literature-based and presently calculated data. Note that data for monoatomic and polyatomic structures are depicted here separately. The diagonal reference line of a perfect match (a slope of 1) is also plotted on this figure as a guide to the eye.

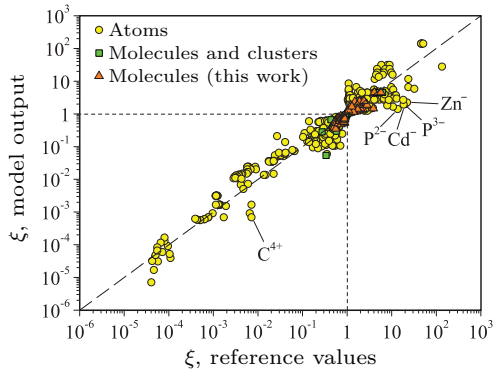


Fig. 6. The ξ values predicted using the optimized model versus the reference ones (symbols, the extreme outliers are labeled explicitly) as well as the dashed line of perfect prediction.

As can be deduced from Fig. 6, with the exception of a few outliers (the worst outliers, for which there is a tenfold or greater difference between the model outputs and the reference data, are C^{4+}, P^{2-}, P^{3-}, Zn^{-}, and Cd^{-}), the concordance between the model-based estimates and reference ξ values is fairly close to the line of ideal performance. In fact, the ratio between the fitted and target ξ values in the vast majority of cases, say, for about 95% of all the data points, does not exceed four times.

As regards the identified worst outliers, it is worth emphasizing that their presence does not necessarily argue against the accuracy of our model, as the reliability of the corresponding data source is to be taken into account in each extreme outlying case.

Indeed, the abscissa of the outlying data point for C^{4+} cation highlighted in Fig. 6 refers to the experimental value of its polarizability given in the 1979 critical review by Shevelko and Vinogradov[16] (0.081 a.u.), while both analytical treatment by Adelman and Szabo[86] and recent coupled-cluster calculations of Wang *et al.*[26] argue in favor of about ten times smaller polarizability for this ion. Besides, the strong discrepancy with the polarizability values of singly charged zinc and cadmium negative ions obtained within the nonrelativistic TDDFT framework by Gould and Bučko[59] cannot be considered a fatal flaw of our model, because even the authors[59] themselves questioned the accuracy of polarizability values they reported for ions of such heavy elements. Only a significant discrepancy with the presumably reasonably accurate polarizability values of doubly and triply negative phosphorus ions P^{2-} and P^{3-} based on high-level coupled-cluster calculations[26] does not appear to be attributable to the quality of the reference data.

Thus, despite the fact the quantity at issue, ξ, varies in magnitude within extremely wide limits, for both anions ($\xi > 1$) and highly charged cations ($\xi \ll 1$) we have an acceptable correlation between ξ as provided by the model and its reference counterpart. The statistical parameters of fitting quality are the following: WRMSD is 0.3094, coefficient of determination R^2 (defined as suggested by Kvålseth.[164]) is 0.931 [both error metrics are calculated for the $\lg(\xi)$ values].

In this connection it is worth noting that this analytical tool as configured, in view of some bias in the reliable fit data toward monoatomic ions of light elements, performs best for charged species containing a small number of electrons, while, as the electron number in the given system increases, the accuracy of the model in describing ionic polarizability slightly (albeit uncritically) deteriorates. This is evident from Table 2, which lists the respective R^2 values for the entire fitting set as well as for its subsets of roughly equal size binned by the number of electrons constituting the given ion.

Table 1. The coefficient of determination R^2 between the model-predicted and reference $\lg(\xi)$ values for the whole data set as well as for its subsets binned by the number of electrons in an ion N.

Subset	R^2
Entire set	0.931
$N \leq 10$	0.993
$11 < N \leq 25$	0.813
$26 < N$	0.796

Meanwhile, the noted feature of the tuned model is not surprising considering the fact that for a significant part of the computational data related to many-electron ions, due to the known difficulties of accounting for relativistic and spin–orbit effects,[13,18,25,26,30,77] the reduced credibility weights w_i were assigned above and, accordingly, the model fitting was less focused on these data.

Additional information about the performance of the model can be extracted from the histogram in Fig. 7, which displays error distribution for $\lg(\xi)$ with the binning interval of 0.1. Note that the error probabilities were calculated by taking into account the above-assigned weights for the data types available.

We see here that the positive and negative deviations of the model outputs from the reference data are almost equally distributed (i.e., no systematic error is observed), and the resulting error distribution over the used data set is quite close to the normal one, although the former is more sharply peaked at the point of perfect prediction (the corresponding Gaussian curve recovered from the WRMSD magnitude indicated above is additionally sketched in Fig. 7).

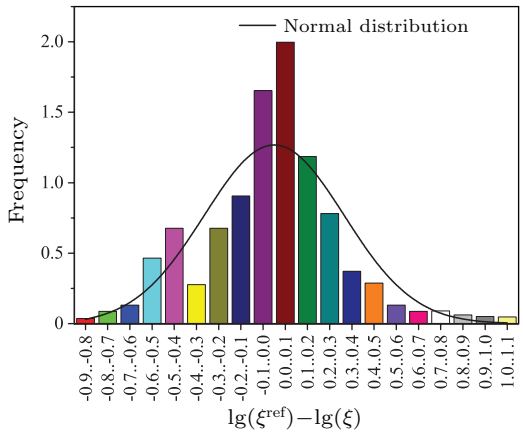


Fig. 7. Histogram of deviations of the logarithmized relative polarizabilities as provided by the developed model with respect to reference data together with the equivalent (in terms of WRMSD) normal distribution (bell curve).

5. A brief guide for the model and data users

Although the model we developed and the data set we employed to set it up were described in detail above, it may well be that those readers who are only interested in the practical use of our model or the ion polarizability data in their work will find it difficult to extract the information they need from this rather lengthy article. Therefore, we give a brief guide to the use of our model and the data we collected in this section, which is intended in a sense to replace the rest of the paper if there is no need to go into the theoretical basis of the model or the details of the data retrieval.

As a matter of fact, the simple semiempirical model proposed in this work makes it possible to readily find the static gas-phase polarizability of the ion of interest (α_i) via the polarizability of the corresponding neutral compound (α_n). To this end, in addition to the polarizability of the uncharged molecule or atom itself (α_n), it is only necessary to specify (i) the number of electrons N and (ii) protons Z constituting the given charged compound, as well as (iii) the sum of the effective numbers of outer (valence) electrons $N_\mathrm{out}^\mathrm{eff}$ of atoms that make up the neutral counterpart of an ion at issue ($S_\mathrm{out}^\mathrm{eff} = \sum N_\mathrm{out}^\mathrm{eff}$).

The evaluation of the effective number of valence electrons for atoms, in turn, is carried out according to expression (3) (see Section 3 above), while for more details the reader can be referred to the original work of Cambi *et al.*[158] or to the tutorial by Carstensen and Dean.[165] With that, although the numbers of electrons and protons must, of course, be integers, the effective numbers of electrons will generally be fractional. In particular, for first-row elements, the $N_\mathrm{out}^\mathrm{eff}$ values are the following: 1.00 (H), 2.00 (He), 1.22 (Li), 2.00 (Be), 2.76 (B), 3.56 (C), 4.39 (N), 5.25 (O), 6.14 (F), 7.04 (Ne). The corresponding values of the input parameters for all of the species considered in this paper are provided in supplementary material.

The final analytical expression for α_i obtained by substituting Eq. (4) into Eq. (2) can be expressed as

$$\alpha_\mathrm{i} = \alpha_\mathrm{n}\left(\frac{N}{Z}\right)^{\frac{p_0 \exp\left[p_1 \frac{N}{Z} + p_2\sqrt{\frac{Z}{N}}(N \bmod 2)\right]}{\left|1-\frac{N}{Z}\right|^{p_3}\left[1+p_4\exp[-p_5(\frac{N}{Z}+p_6\ln\frac{Z}{S_\mathrm{out}^\mathrm{eff}}+p_7)^2]\right]}} \cdot \frac{Z^{p_8}}{\left(S_\mathrm{out}^\mathrm{eff}\right)^{p_9}}, \quad (5)$$

where $p_0, \ldots, p_9$ are optimized values of dimensionless fitting parameters of the model. Specifically, the following set of adjustable model parameters is recommended for use: $p_0 = 6.141$, $p_1 = 0.074$, $p_2 = -0.494$, $p_3 = 0.464$, $p_4 = 3.030$, $p_5 = 15.722$, $p_6 = -1.005$, $p_7 = -0.257$, $p_8 = 0.420$, $p_9 = 0.605$. Note that the binary (modulo-2) division of N returns 0 for ions with an even number of electrons and 1 otherwise.

We stress that the developed model has no limitations on the size, charge, and elemental composition of the ions in question, but it is worth noting that if there is no analogous neutral component for the ion of interest, as, say, for the H_3^+ cation, our proposed model is unfortunately inapplicable.

Regarding the accuracy of the model, the following can be said. With the exception of a few severe outliers, the concordance between the model-based estimates and reference ion polarizability values is fairly good, *viz.* the ratio between the fitted and target relative polarizability values $\xi = \alpha_\mathrm{i}/\alpha_\mathrm{n}$ in most cases, say, for about 70% of all the data points, does not exceed two times.

Note in this connection that a deviation of less than two times can really be considered satisfactory for such a quantity as ion polarizability because the polarizability of a multielectron system with electron attachment (detachment), as is known, can vary over orders of magnitude. In addition, it should be realized that the polarizability of ions (especially, anions) is a quantity that is generally known with not very high precision. Indeed, for some negative monoatomic ions, the discrepancy among different theoretical estimates of polarizability can reach several times.[28–30,44,51,59,75,82]

As for a few extreme outliers, the difference between the model outputs and the reference data for them may be tenfold or more, however, in most of these specific cases, the validity of the data we have taken for reference is seriously questioned (see for the related discussion in Section 4).

As concerns the possible reuse of our collected and calculated data on the polarizability of ions and their corresponding neutrals, they are all provided in the data sheets of Supplementary material (in atomic units, i.e., Bohr cubed) along with the corresponding literature references and indication of the method of obtaining. The dipole moment values (in Debye) computed in passing for the ions for which we performed our own DFT polarizability calculations are also given in the Table S2 of supplementary material.

6. Concluding remarks

The eventual outcome of this work that deserves to be highlighted is a simple analytical model for predicting the

static isotropic polarizability of arbitrarily charged ions of any size and elemental composition. Our model allows one to readily estimate the relative increase (decrease) in the gas-phase polarizability of a multielectron system upon electron attachment (detachment) by means of a couple of straightforward expressions: (i) Eq. (4) for the effective variable β that determines, within the semiclassical picture, the extent to which ionization degree (the ratio of number of electrons in a system to number of protons) affects polarizability and (ii) Eq. (2) that for a given value of effective variable β returns the desired ratio of the polarizability of an ion to that of its neutral counterpart.

This compact model is based on some theoretical assumptions and a number of established (both previously and in this work) regularities in polarizability of ionized atoms and molecules. With that, the presence of several free parameters in Eq. (4) allows adjusting the proposed model to match the known body of data on the polarizability of charged particles. To this effect, we adopted the results of numerous theoretical calculations and measurements reported in the past and thus assembled a diverse and representative set of gas-phase polarizability values of 250 individual monatomic and polyatomic ions (overall, 465 literature data points). To counteract the appreciable bias in the literature data toward monoatomic ions, for extra 76 molecular ions of general concern, for which there are practically no data available, we additionally performed our own coupled-perturbed Kohn–Sham calculations.

Incidentally, the data set for polarizability of ions that we assembled has a stand-alone value for future research and, in particular, can be used for further "stress-testing" of DFT approximations as well as *ab initio* wave function methods for proper description of electron density.

As a result, the simple physically motivated model we formulated and adjusted has reasonable (given the substantial uncertainties in the reference data discussed above) accuracy in predicting the static polarizability of ions of any size and charge. It requires as input data, apart from the total numbers of electrons and protons, only the elemental composition of the ion, leaving aside the knowledge of the intrinsic nature of the electronic structure of the electron-deficient and electron-rich systems at issue.

We believe that the predictive power of the created analytic tool should suffice for the applications where there is a pressing need for rapid low-cost estimation of polarizability in relation to a large set of atomic, molecular, and cluster ions. The developed model can also be helpful for critical evaluation of known and at times conflicting experimental and theoretical data on the electric properties of charged species and thus for making appropriate consensus recommendations.

To conclude, it is worth noticing that, to the best of the authors' knowledge, no such models have been created so far, and therefore the present effort in this direction may be regarded as a "trial balloon". Assuredly, we cannot claim that the analytical model of this work is final and complete. On the contrary, it is open for subsequent recalibration taking into account credible past findings that unfortunately escaped our attention (if any) and future available data of theoretical or experimental origin, especially since all the necessary source data are publicly accessible both as supplementary material to this article in the PDF format and as data sheets allocated in the Science Data Bank as well. Moreover, some revision of the assumptions underlying the model and, accordingly, its redesign may also be required in the light of new evidence.

Data availability statement

The data that support the findings of this study are openly available in Science Data Bank via the link https://doi.org/10.57760/sciencedb.07526.

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