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Analysis of oxide dielectric data and the quantum theory of atomic polarizability

N W Grimes[†] and Robin W Grimes[‡]

[†] Department of Physics, Aston University, Birmingham B4 7ET, UK

[‡] Department of Materials, Imperial College, London SW7 2BP, UK

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Abstract. Ion polarizabilities derived from low-frequency precision measurements of the dielectric constants of single crystals of more than 120 different oxides have recently been published but have proved difficult to interpret in terms of classical theory. The latter predicts that the polarizability of an ion should be proportional to the cube of its radius. We present a new approach to the analysis of the experimental data which clearly demonstrates a square law dependence, in agreement with the quantum mechanically based result expected for a purely electronic polarizability. There is then a demonstrable relationship between the low-frequency polarizability of an ion and the orbital angular momentum quantum number associated with its outermost, or most polarizable, electron subshell.

The apparent absence of ion displacement contributions in oxides is explained as a consequence of the method though which polarizability data have been derived and the relative magnitude of the Szigeti charge.

The new analysis offers, for the first time, the possibility of deriving a set of absolute values for the low-frequency ‘in crystal’ polarizabilities of all ions for which there is a clearly established valence state. These should permit more reliable calculations of the properties of dielectric materials and a useful check for the modelling of their dynamical behaviour.

1. Introduction

The current importance of developments in the optical transmission of information and in advanced computers has led to intense interest in the related properties of certain significant materials, notably oxides, and especially in their dielectric behaviour. Progress has been hampered, however, partly as a consequence of a lack of good experimental data and partly through inadequate theoretical understanding.

Recently, a useful improvement in the quality of dielectric data for oxides has been achieved by insisting on precision measurements from single-crystal samples of high purity and cubic symmetry [1, 2]. Data from non-cubic crystals were only included if the dielectric anisotropy was known.

Numerous checks on the internal consistency of this data set have been made [3–7] by testing against the concept of the additivity of molecular polarizabilities as in, for example,

$$\alpha_D(M_2M'O_4) = \alpha_D(M'O) + \alpha_D(M_2OssConmt_3). \quad (1)$$

For this purpose it was assumed that the low-frequency or dielectric polarizability, α_D , could be derived from the measured dielectric constant, ϵ_0 , through the Clausius–Mossotti equation

$$\alpha_D = \frac{3V_m(\epsilon_0 - 1)}{4\pi(\epsilon_0 + 2)} \quad (2)$$

where V_m is the volume per molecule and ϵ_0 is measured in the range 1 kHz–10 MHz. This work has shown that, despite the neglect of a contribution from ion displacements in equation (2) (in section 5 we consider the validity of this approximation), the difference between the two sides of equation (1) is typically no more than 0.5–1.5% for a remarkably extensive series of aluminates, beryllates, borates, gallates, silicates and phosphates. Deviations greater than this could usually be traced to ferroelectricity, to ionic or electronic conductivity or to the presence of impurities or other defects.

Some progress has also been achieved towards a deeper understanding of the factors which determine dielectric behaviour by consideration of the concept of molecular polarizabilities of complex substances as a sum of the constituent ion polarizabilities

$$\alpha(\text{AB}_2\text{X}_4) = \alpha(\text{A}^{2+}) + 2\alpha(\text{B}^{3+}) + 4\alpha(\text{X}^{2-}) \quad (3)$$

(for reasons explained below we assume that the ion polarizabilities involved here are those appropriate to the environments provided by the structure of the material). Ion polarizabilities, in principle, can be related to fundamental theory and are therefore potentially powerful for analytical purposes but the decomposition of the sum is not straightforward. At high frequencies, where extensive experimental data in the form of refractive indices have been available for some time, a common practice has been to fix the polarizability of one ion, for example by reference to theory, and then to derive the polarizabilities of other ions on the basis of best fit to the data. This was the method employed by Tessman *et al* [8] to analyse the optical behaviour of the alkali halides and alkaline earth chalcogenides. They chose to fix α_∞ for Li^+ with the idea that even a large percentage error on such a small polarizability would lead to relatively smaller errors in the polarizabilities of the larger ions. Variations on this method were subsequently used by various authors [9–11] and many different sets of empirical *electronic* ion polarizabilities, α_∞ , have now been derived.

In this paper we are concerned with the interpretation of experimental results at low frequencies, that is, with *dielectric* ion polarizabilities, α_D . We consider in particular the data set derived by Shannon [2] using a least-squares fitting procedure and accurately determined dielectric constants from the single crystals of more than 120 different oxides and 25 fluorides. These values substituted into equation (3), it is to be noted, reproduce the molecular polarizabilities of many of the compounds considered to an accuracy of about 1.0%.

As before, the values obtained for the ion polarizabilities depend to some extent on the choice of reference. Shannon chose $\alpha_D(\text{B}^{3+}) = 0.05 \text{ \AA}^3$, which resulted in a value for α_D for O^{2-} of 2.01 \AA^3 . This is somewhat lower than had previously been supposed. On the other hand, if α_D for O^{2-} is much higher, the polarizabilities for B^{3+} and Be^{2+} come out negative. Thus, acceptable polarizability values are limited to within quite a small range and, when this fact is added to the predictive quality noted in the previous paragraph, it is clear that there is a need for a proper basis for interpretation.

Classically, the polarizability of an ion is expected to be equal to the cube of its radius, r (see, for example, the book by Dekker [12]), but which value of radius should be chosen is not clear. Traditional ionic radii used by crystallographers are based on the assumption that $r(\text{O}^{2-}) = 1.40 \text{ \AA}$ and very comprehensive tables of such radii [13] are now well established. These radii, however, do not provide a good fit to the polarizability data and it has been argued that the so called crystal radii [13], which are based on $r(\text{O}^{2-}) = 1.26 \text{ \AA}$ and $r(\text{F}^-) = 1.19 \text{ \AA}$, are more appropriate. Figure 1 shows that even then the scatter of the experimental data is considerable, with the negative ions almost in accord with classical expectations ($\alpha_D = r^3$) but positive ions clustered about a line of much steeper slope—see the remarks in section IIIB of the article by Shannon [2].

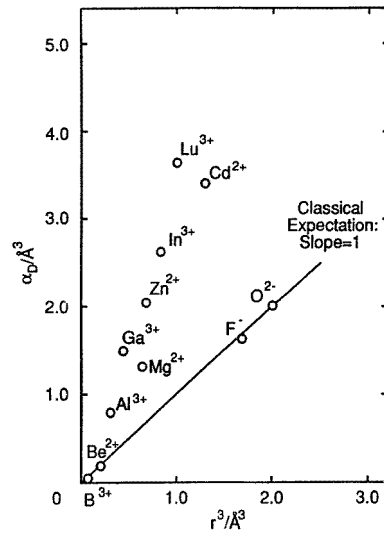


Figure 1. Dielectric ion polarizability α_D , according to Shannon [2], as a function of the cube of the crystal radius of the ion concerned: data for the latter are taken from Shannon [13].

Finally, it is worth noting that there also exists a good quantum theory of atomic polarizability [14–16], which seems to have been largely neglected—perhaps because it is seen as too complicated or not directly amenable to comparison with experiment. However, given the high quality of the new experimental data and the failure of the classical interpretation, there is an impetus to reconcile these results with the predictions of the quantum based model. It is the purpose of this paper to suggest means of overcoming the outstanding difficulties of interpretation and to present a first step towards this reconciliation.

2. Choice of data set

As explained in the introduction, the starting point for our paper is the set of experimental dielectric constants reviewed by Shannon [2] and, in particular, the values he thereby derived for the dielectric polarizabilities of 60 different ions from the periodic table (for present purposes we ignore OH^-). An interesting feature of this analysis is that, despite acceptance of the possibility that environmental effects might be important, it was shown that the assumption of a variable oxygen polarizability (dependent on nearest-neighbour distance) generally produces no more than a second-order correction to values derived by assuming all ions possess a constant dielectric polarizability. The data summarized in column 2 of our table 1 are therefore taken from column 2 of table III of Shannon [2]. However, as we seek to correlate ion polarizabilities with their corresponding ionic radii and the latter are known to possess significant environmental (i.e. co-ordination number) dependence [13], it may be that the set of polarizabilities should have been derived with cations (as well as oxygen ions) having different co-ordinations distinguished.

In column 3 of our table 1 we list the traditional crystallographic ionic radii of the ions concerned (as each ion polarizability probably corresponds to some kind of average over a variety of environments dominated by six fold co-ordination, we use the radii for six fold co-ordination only) from the revised tables given by Shannon [13]. This collection of radii, derived from analysis of the bond distances found in almost 1000 crystal structures,

Table 1. Ion polarizability data and modified crystal radii.

Ion	Pol. α_D (\AA^3)	Trad. Ion radius (\AA)	Modified crystal radius, r (\AA)	r^2 (\AA^2)
Li ⁺	1.20	0.76	0.96	0.922
Be ²⁺	0.19	0.45	0.65	0.423
B ³⁺	0.05	0.27	0.47	0.221
O ²⁻	2.01	1.40	1.20	1.440
F ⁻	1.62	1.33	1.13	1.277
Na ⁺	1.80	1.02	1.22	1.488
Mg ²⁺	1.32	0.720	0.920	0.846
Al ³⁺	0.79	0.535	0.735	0.540
Si ⁴⁺	0.87	0.400	0.600	0.360
P ⁵⁺	1.22	0.38	0.58	0.336
K ⁺	3.83	1.38	1.58	2.496
Ca ²⁺	3.16	1.00	1.20	1.440
Sc ³⁺	2.81	0.745	0.945	0.893
Ti ⁴⁺	2.93	0.605	0.805	0.648
V ⁵⁺	2.92	0.54	0.74	0.548
Zn ²⁺	2.04	0.740	0.940	0.884
Ga ³⁺	1.50	0.620	0.820	0.672
Ge ⁴⁺	1.63	0.530	0.730	0.533
As ⁵⁺	1.72	0.46	0.66	0.436
Rb ⁺	5.29	1.52	1.72	2.958
Sr ²⁺	4.24	1.18	1.38	1.904
Y ³⁺	3.81	0.900	1.100	1.210
Zr ⁴⁺	3.25	0.72	0.92	0.846
Nb ⁵⁺	3.97	0.64	0.84	0.706
Cd ²⁺	3.40	0.95	1.15	1.323
In ³⁺	2.62	0.800	1.000	1.000
Sn ⁴⁺	2.83	0.690	0.890	0.792
Cs ⁺	7.43	1.67	1.87	3.50
Ba ²⁺	6.40	1.35	1.55	2.40
Lu ³⁺	3.64	0.861	1.061	1.126

is believed to be reliable to about $\pm 0.01 \text{ \AA}$ or better in the sense that they may be used to predict unknown bond distances with this order of confidence. However, as Fumi and Tosi [17] point out, the traditional radii do not have a good theoretical basis and, from a fundamental point of view, one should perhaps expect better correlation with the crystal radii as, indeed, was found by Shannon.

Shannon and Prewitt [18] have commented that the crystal radii only differ from traditional radii by a constant viz. 0.14 \AA —crystal radii for negative ions being smaller by this amount and crystal radii for positive ions larger by the same quantity (the asymmetrical treatment preserves agreement with experimentally determined bond lengths). These values are believed to be closer to having absolute significance [13] but may still be not quite right, i.e. there is scope for refinement of the correction constant. In section 4 we argue that this possibility provides the natural parameter to optimize fit between theory and experiment. The optimization procedure thus leads to a set of modified crystal radii and these are listed

in column 4 of table 1. At this point it is sufficient to note that the latter differ from the related traditional radii by 0.20 Å (i.e. correspond to a further correction of 0.06 Å) with the same sense as occurred with the previously accepted list of crystal radii.

3. The basis of the new analysis

The most complete quantum theory of *atomic* polarizability is that of Buckingham [16], in which such polarizabilities were calculated from Hartree self-consistent wave functions by a method based on a perturbation treatment of the effect that an external uniform electric field has on such a wave function. Despite the use of Hartree wave functions (which were obtained without recourse to electron exchange), Buckingham's expression accounts for the change in the exchange interaction due to the external field. In the present analysis, however, the simpler results of Slater and Kirkwood [14] and of Hellmann [15] are used. For atoms or ions with closed shell electronic configurations they are given respectively as limiting cases (i.e. ignoring the contribution from exchange) by Buckingham in the form

$$\alpha_D = \frac{4a_0^3}{9N} \left\{ \sum_{n,\ell} v_\ell \langle r^2 \rangle_{n\ell,n\ell} \right\}^2 \quad (\text{IA})$$

$$\alpha_D = \frac{4}{9} a_0^3 \sum_{n\ell} v_\ell \langle r^2 \rangle_{n,\ell,n\ell}^2 \quad (\text{IIA})$$

where the expectation value $\langle r^2 \rangle$ is expressed in atomic units, n and ℓ are principal and orbital angular momentum quantum numbers respectively, $v_\ell = 2(2\ell + 1)$ and a_0 is the radius of the first Bohr orbit of hydrogen in ångströms.

The summations in these equations are over all the electron subshells, but if it can be assumed that the outermost subshell makes the predominant contribution (some sources claim more than 90% of contributions to polarizability originate from the outermost shell [19, 20], a claim for which there is a good theoretical basis, see the appendix), then both (IA) and (IIa) simplify to

$$\alpha_D = \frac{4}{9} a_0^3 2(2\ell + 1) [\langle r^2 \rangle_{n,\ell}]^2 \quad (4)$$

where, in this case, quantum numbers n, ℓ refer to the outermost subshell. Equation (4) may then be re-arranged in the following manner

$$\alpha_D = \frac{8}{9} a_0 (2\ell + 1) [a_0 \langle r^2 \rangle]^2. \quad (5)$$

As we show in what follows and in our following paper (in preparation), it is equation (5)—essentially the contribution to electronic polarizability of a single subshell—which provides the new means for interpretation of the experimental dielectric data. In section 4 the result is used to provide an immediate analysis for those ions which satisfy the assumed closed shell electronic configuration. Our following paper then describes how equation (5) may be modified to deal with cases where there are contributions from incomplete or several subshells.

4. Application to ions with closed shell electronic configurations

There is an important general point concerning equation (5) which should be emphasized in relation to the squared factor, $[a_0 \langle r^2 \rangle]^2$. As demonstrated in our appendix, it would be

more correct to write this expression in the form

$$[a_0^2 \langle r^2 \rangle] \langle r^2 \rangle$$

because, strictly, it is a mean square radius for the electronic subshell concerned multiplied by a dimensionless factor which arises from an oscillator strength. Overall, it may be interpreted as a weighted mean square radius (in square ångströms if a_0 is in ångströms) which, as such, is not a directly accessible physical parameter. Nevertheless, it seems reasonable to suppose that this form of mean square radius for an outer electron subshell could be related to the square of a conventional ionic radius.

Therefore there is the implication from equation (5) firstly that polarizabilities derived from experimental dielectric data should be plotted against the *square* of an appropriate ionic radius rather than the cube (if contributions from ion displacements can be neglected—see section 5), and secondly that one should optimize the fit through a systematic variation in ion size.

Noting from Shannon's experience that crystal radii rather than traditional radii correlate better with polarizability data [1] and that these two measures of ionic size differ only by a constant, as explained in section 2, it is plain that this constant provides the natural parameter to be optimized. The different ionic radii are then, indeed, simultaneously varied in a systematic way, for agreement with experimental bond lengths is maintained. Thus the polarizability data have been fitted to the square of the modified crystal radii, the correction to crystal radii having been derived through the optimization process described.

Figure 2 shows that the method leads to good agreement with the form of equation (5), the experimental data being revealed as belonging to one or other of a quantized series of straight lines whose successive slopes corresponding to $\ell = 0, 1, 2, 3$, are given by

$$\frac{8}{9} a_0 (2\ell + 1)$$

i.e. the ion polarizabilities of Shannon *et al* are seen to provide direct experimental evidence to support the quantum mechanical model. The problem of the apparently different behaviour of the positive and negative ions, noted by Shannon [1, 2] is, moreover, simultaneously resolved, but the apparent absence of ion displacement contributions to the *total* polarizabilities needs to be explained.

5. Discussion

According to the analysis used by Sangster and Stoneham to interpret the dielectric behaviour of oxides with rocksalt structure [21], the sum of the low-frequency anion and cation polarizabilities in those compounds is given by

$$(\alpha_1 + \alpha_2) = \alpha_\infty + F_0^{-1} (Z - Z')^2 \quad (6)$$

where

$$\alpha_\infty = \frac{3V_m}{4\pi} \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right) \quad (7)$$

$$F_0 = \frac{\mu w_o^2}{e^2} \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \quad (8)$$

and ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, w_o the transverse optical frequency (see, for example, the book by Cochran [22]), μ the reduced mass, Z the ionic charge and Z' the Sziget charge (as defined by Sangster *et al* [23]). In this scheme the right-hand side of equation (6), $\alpha_\infty + (Z - Z')^2/F_0$, represents the sum of

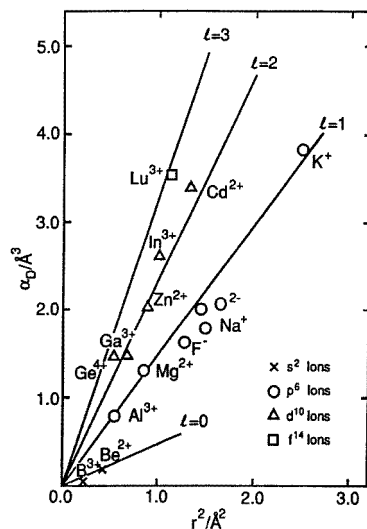


Figure 2. Dielectric ion polarizabilities, α_D , as a function of the square of the modified crystal radii. Note that the straight lines in this figure are theoretical predictions for $\ell = 0-3$ according to equation (5)—see the text.

the high-frequency polarizabilities and a correction term related to the ion displacements respectively. The left-hand side of equation (6), so determined, is then taken to be a sum of *free ion* polarizabilities.

By contrast, Shannon's ion polarizabilities were derived through the use of the Clausius–Mossotti equation (equation (2) of this paper) and it is by no means clear that his analysis should give results comparable to those of Sangster and Stoneham. The theoretical basis for the latter is explained by Sangster *et al* [23] from whose equations (8) and (12) it can be deduced that

$$\frac{3V_m}{4\pi} \left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \right) = (\alpha_1 + \alpha_2) + \frac{2Z}{F_0} (Z' - Z/2). \quad (9)$$

Thus it appears that Shannon's ion polarizabilities are flawed through the systematic neglect of the second term of the RHS of equation (9) which is part of the ion displacement contribution to low-frequency polarizability. The importance of this second term, however, depends on the factor $(Z' - Z/2)$ whose sign is determined by the relative magnitude of the Szigeti charge Z' . Sangster and Stoneham show that with oxides, where $Z = 2$, Z' is sometimes larger and sometimes smaller than $Z/2$ —see column 1 of table 2. If individual ion polarizabilities are deduced using the dielectric constants from a range of compounds, where the ion displacement contribution is sometimes positive and sometimes negative, it is evident that these deduced values can then be nearly free of contamination by displacement terms despite the use of the Clausius–Mossotti equation. In this way the good quantitative agreement between our theoretical model and the ion polarizability values derived by Shannon may be understood.

Detailed inspection of table 1 reveals that, nevertheless, there are some discrepancies between Shannon's empirical results and the predictions of our model. In particular, polarizabilities of ions supposed to possess larger valencies such as Y^{3+} , Si^{4+} , Zr^{4+} and V^{5+} appear to be a rather poor fit. It is possible that these higher valence states do not truly exist and, in fact, that such large deviations indicate the presence of covalency or some

Table 2. The calculated sum of ion polarizabilities for oxides in cubic ångströms: a comparison with the work of Sangster and Stoneham [21].

	Z'	S and S ($\alpha_1 + \alpha_2$) Eq. (6)	($\alpha_1 + \alpha_2$) Eq. (5)
MgO	1.198	2.466	3.22
CaO	1.177	3.986	4.06
SrO	1.191	5.021	4.72
BaO	1.376	5.768	5.42
MnO	1.033	4.269	4.28 ^a
FeO	0.890	4.477	4.11
CoO	0.934	3.995	4.00
NiO	0.858	4.059	3.82

^a Polarizabilities for transition ions taken from our next paper.

similar complicating factor as has been proposed in SiO₂ [24]. On the other hand, it is probably more significant that oxide structures formed with these ions tend to have local environments with other than six fold co-ordination (see section 2).

Other sources of discrepancy may be associated with an erroneous assumption of an r^3 law or with erroneous inclusion of ferroelectric compounds in the dielectric data set. In [6], for example, the polarizability of Fe³⁺ is obtained using the oxide additivity rule (as in e.g. equation (1)) and by averaging over three ferrite compounds. Two of the latter (also included in [2]), however, crystallize with the spinel structure and are believed to possess permanent dipole moments [25–27]. As we show in our next paper [21], Shannon's value for the polarizability of Fe³⁺ seems to be too high.

There remains the question of the interpretation which should be given to the polarizability sums ($\alpha_1 + \alpha_2$). Since in our theory each of the polarizabilities involved is derived from a corresponding *in crystal* ionic radius we take the view that the resultant sums must be sums of *in crystal* polarizabilities. As noted previously, Sangster *et al* [23] interpret the same quantities which they derive for the alkali halides as *free ion* sums, but this is difficult to accept as equation (6) shows explicitly that ($\alpha_1 + \alpha_2$) contains a part of the ion displacement contribution to low-frequency polarizability. (The full displacement contribution is Z'^2/F_0 as may be seen by substituting for ($\alpha_1 + \alpha_2$) in equation (9).) Indeed, as Sangster and Stoneham [21] realized, the polarizability sums ($\alpha_1 + \alpha_2$) from oxides are too high to be free ion values. Therefore we believe that the sums derived in [23] for the alkali halides are also *in crystal* values.

Further support for the *in crystal* interpretation is given by the polarizability sums ($\alpha_1 + \alpha_2$) obtained by Sangster and Stoneham using equation (6) and the experimental data for the compounds they considered (shown in column 3 of table 2). With the exception of MgO, there is a good correspondence between their results and the related sums calculated from our model which appear in column 4.

Given that ($\alpha_1 + \alpha_2$) is an *in crystal* sum, environmental effects are to be expected, and to take these into account through the procedure described by Sangster *et al* [23] is not straightforward. In this respect, the calculation using ionic radii can be shown to have considerable advantages. Not only are the effects of co-ordination number already well established [13] but, since the electronic contribution to molecular polarizability is calculated separately for each ion in our model, it is evident that this method is easily

extended to cover (cubic) compounds where ions occur with a variety of environments. Provided experimental data are then available to determine F_0 and the Szigetti charge, Z' , the low-frequency dielectric constant may be derived through a suitably modified form of equation (9).

Because in our analysis Shannon's polarizability data have been directly related to quantum theory, albeit in simplified form, it is evident that there is now the basis for achieving a data set with absolute significance. This has some importance, for example, for the modelling of defect properties where the reliability of predictions has been shown to depend sensitively upon the quality of the interatomic potentials used in the simulations [29, 30]. In this context, it is worth noting that the property of transferability so valuable for defect calculations [21, 28] is retained by polarizability in our model, if proper respect is paid to co-ordination.

We note, finally, that there is a more than superficial resemblance between our theory and the shell models used to describe lattice dynamical behaviour. Shell charges found from fitting the latter to experimentally determined phonon dispersion curves tend to be smaller than the charges associated with the outermost electronic subshell (see, for example, [23]) but it may be that further investigation will reveal a closer connection. The present results should thus provide a useful check for the modelling of the dynamics of dielectric materials.

Acknowledgment

It is a pleasure to acknowledge the interest and useful comments of Professor A M Stoneham FRS.

Appendix

According to classical theory for free ions (see Kittel [31], for example) the low-frequency or dielectric polarizability *per electron* is given by an expression of the form

$$\alpha_D = \frac{e^2}{m w_k^2} \quad (\text{A1})$$

where e and m are electronic charge and mass respectively and w_k is an absorption frequency. This is equivalent to writing

$$\alpha_D = \frac{e^2 \hbar^2}{m W_k^2} = \frac{e^4}{W_k^2} a_0 \quad (\text{A2})$$

as the first Bohr radius of hydrogen $a_0 = \hbar^2 / m e^2$. W_k is then the energy of the state corresponding to resonant frequency w_k .

If the dipole moment here is imagined as arising from the application of a low-frequency electric field in, say, the x -direction, it is plain that equation (A2) could also be re-written as

$$\alpha_D = a_0 [x^2].$$

Thus, in terms of the mean radius, r , of the electron orbit concerned, if

$$r^2 = x^2 + y^2 + z^2$$

and statistically,

$$[x^2] = [y^2] = [z^2] = \frac{1}{3} [r^2]$$

where square brackets denote a time average, equation (A2) becomes

$$\alpha_D = \frac{1}{3}a_0[r^2]$$

i.e.

$$\alpha_D = \frac{1}{3}a_0^3[r^2] \quad (\text{A3})$$

if r is expressed in dimensionless atomic units.

As emphasized previously, this is the dielectric polarizability *per electron*. For an electron subshell with $2(2\ell + 1)$ electrons, the dielectric polarizability is

$$\alpha_D = \frac{2}{3}a_0^3(2\ell + 1)[r^2]. \quad (\text{A4})$$

For the corresponding result in quantum theory (the Kramers–Heisenberg dispersion formula) we observe firstly that the time average $[r^2]$ should be replaced by the matrix element of the same quantity for the k th electronic transition [32] i.e. $\langle r^2 \rangle$, where

$$[r^2] = 2\langle r^2 \rangle. \quad (\text{A5})$$

Secondly, the quantum expression includes a factor f_k , which is the *oscillator strength* for the electronic transition corresponding to frequency w_k , where

$$f_k = \frac{2m}{e^2\hbar} w_k M_{km}^2 \quad (\text{A6})$$

and M_{km} is the matrix component of the dipole moment between states k and m .

Note that quantity f is *dimensionless* i.e. *a pure numerical fraction*. Indeed, a well known result in quantum theory, the *sum rule*, states that for a given atom ‘the sum of the oscillator strengths over all possible electronic transitions equals unity’, i.e.

$$\sum_k f_k = 1.$$

By substituting for M in equation (A6) it is possible to re-express this equation in the form

$$f_k = \frac{2}{3}\langle r^2 \rangle \quad (\text{A7})$$

where $\langle r^2 \rangle$ here is again dimensionless.

If now both (A5) and (A7) are incorporated into equation (A4) it is easily seen that this equation in quantum form must be

$$\alpha_D = \frac{4}{3}a_0(2\ell + 1)[a_0^2\langle r^2 \rangle]f_k \quad (\text{A8})$$

which, after substituting for f_k , comes out as

$$\alpha_D = \frac{8}{9}a_0(2\ell + 1)[a_0\langle r^2 \rangle]^2 \quad (\text{A9})$$

i.e. identical to equation (5) of section 3. Note, however, that the second dimensionless factor $\langle r^2 \rangle$ has arisen from f_k , the oscillator strength. Thus the contribution to the polarizability of the atom from the electronic subshell concerned is proportional to its mean square radius. There is no theoretical basis in quantum theory for assuming a cube law.

The reason for the dominance of the contribution of the outermost electron subshell to the polarizability of an ion, exploited in section 3, is now also made plain. To echo the words of a remark from many years ago [33] ‘In the sum (over all orbits—our equation (5)), one term, corresponding to the principal absorption from the ground state, generally makes by far the largest contribution. That is, its oscillator strength f_k is somewhat near unity, the others being much smaller’.

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