

The static dipole polarizability of aluminium atom: discrepancy between theory and experiment

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Abstract

A serious discrepancy of almost 20% has been found between the experimentally measured static dipole polarizability of aluminium atom and very exhaustive theoretical calculations. This fact is important because in some experimental works the dipole polarizability of atomic clusters is measured with respect to the one of aluminium atom.

1. Introduction

The static dipole polarizability is an important quantity in many branches of physics and chemistry [1,2]. Therefore, for a long time effort has been put in order to understand better its characteristics and to develop theoretical as well as experimental techniques to know its value in a variety of electronic systems. In the field of atomic clusters the dipole polarizability has become one of the most important known quantities to guess the geometry of the clusters [3]. Usually, the experimental measurement is conducted using a molecular beam apparatus equipped with a position-sensitive time-of-flight mass spectrometer. An expanding free jet cluster is skimmed into a beam which passed through a linear gradient electric deflection pole assembly [2,3]. The cluster beam deflection is proportional to the dipole polarizability, the strength of the electric field and its gradient as well as to some geometrical parameters. Since most of the times some of this parameters are not known the dipole polarizability is evaluated using some standard system to calibrate the measure. Usually atomic sodium or aluminium are used. Hence, an accurate value

of their polarizabilities are needed. Surprisingly, the atomic dipole polarizability of aluminium atom presented in the review by Miller and Bederson [1], which is informed to have an error of around 2% differs in almost 20% with the experimental value [4] used in the subsequent experiments in atomic clusters [5]. Miller and Bederson refer to the theoretical value of Reinsch and Meyer [6] of 56.27 a.u. whereas the experimental value used in the cluster experiments is of 45.9 ± 2 a.u. Considering that serious discrepancies have been found between the experimental and the theoretical values of the dipole polarizability of lithium [7,8] and silicon clusters [9,10], it seems important to examine the issue in more detail. To our knowledge no new calculations including electron correlation have been published, and one has to rely only in the near Hartree-Fock values calculated by Stiehler and Hinze [11].

The reliability of the theoretical methods to calculate atomic polarizabilities has been many times confirmed. One can mention two examples. Very recently an accurate measurement of the dipole polarizability of cesium atom has been published [12]. It puts the error bar lower than 1%, and there are at least four independent theoretical calculations within this error bar [13]. Sodium atom is also usually used as standard. Here, the new theoretical calculations by Maroulis [14] yields a value of

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165.06 a.u. to be compared with the experimental value informed by Ekstrom et al. [15] of 162.7 ± 0.8 a.u. The deviation is of around 1%.

The aim of this communication is to provide exhaustive theoretical calculations of the dipole polarizability of aluminium atom. The calculations rely on the finite field method, where the second derivative of the energy with respect to the electric field is calculated numerically as implemented in the GAUSSIAN 98 package of programs [16]. The electronic structure calculations started at the unrestricted Hartree–Fock level (UHF) and then the electron correlation is added. In Table 1, the convergence of our results with respect to the correlation level of calculation is shown. All the electrons were correlated. One can see, that using the Moeller–Plesset perturbation theory, the result changes in less than 0.5 a.u. in going from third to fourth order of perturbation. At the coupled cluster level of calculation the effect of correcting for triple excitations has a negligible effect. Hence, it seems that at the coupled cluster level considering single, double and an estimate of connected triple excitations, CCSD(T) the most important correlation effects are included and the error due to the lack of correlation should be of less than 1 a.u. In the following, this will be the method used in the calculations. It is well known that the dipole polarizability is very sensitive to the quality of the basis set [6]. Therefore, a clear procedure to obtain high quality basis sets is necessary. In this work, as starting point standard high quality basis sets have been used. They are the 6-311++G(3df,3dp) implemented by Pople et al. [17], the aug-cc-pVTZ, the aug-cc-pVQZ and the aug-cc-pV5Z constructed by Dunning et al. [18], they will be denoted basis A, B, C and D, respectively. In a more traditional notation basis set A is of the type 14s10p3d1f/[7s6p3d1f], basis set B of the type 42s17p3d2f/[6s5p3d2f], basis C of the type 43s20p4d3f2g/[7s6p4d3f2g] and basis D of the type 53s21p5d4f3g2h/[8s7p5d4f3g2h]. Then, new exponents were added taking a half of the smallest one for the corresponding angular momentum. The exponent of the g-symmetry function for basis A and B was varied in the range of 0.05–0.40 trying to maximize the value of the dipole polarizability. The new basis sets and their

Table 1
Convergence of the dipole polarizability of aluminium atom (in a.u.) with respect to the correlation level^a

Correlation level	$\langle\alpha\rangle$
MP2	60.10
MP3	59.36
MP4	58.89
CCD	58.49
CCSD	58.48
CCSD(T)	58.44

^a All calculations with the aug-cc-pvQZ basis set.

notations are collected in Table 2. The calculated average dipole polarizability is informed in Table 3. One can observe some important points. At each stage of basis set developing, the four basis sets, A, B, C and D give similar results with a deviation less than 1 a.u. After adding the first diffuse function of f-symmetry the values are rather stable demonstrating a convergence of the results. The addition of a function of g-symmetry has almost no influence in the results. At the Hartree–Fock level basis set A1, B1 and D1 yield 61.17, 61.25 and 61.23 a.u., respectively, in good agreement with the numerical near Hartree–Fock value of 62.05 a.u. which was calculated at the restricted Hartree–Fock level explaining perhaps the small deviation. Usually, the anisotropy is more sensitive to the basis set. Using the greatest basis set, D1, at the Hartree–Fock level, one obtains an anisotropy of 27.77 a.u. in comparison with the value of 28.91 a.u. reported by Stiehler and Hinze [11]. It is also important to mention the negligible importance of correlating all the electrons. Keeping frozen the core electrons yields a polarizability of 58.72 against 58.69 a.u. for the full calculation for the basis set B. On the other hand, the influence of the triple excitations is also almost negligible corroborating the results

Table 2
Description of the basis sets

A: 6-311++G(3df,3pd)
A1: A + sp = 0.016; d = 0.040; f = 0.0291
A2: A1 + sp = 0.0080; d = 0.020; f = 0.0150
A3: A2 + g = 0.100
B: aug-cc-pVTZ
B1: B + sp = 0.073; d = 0.0178; f = 0.043
B2: B1 + sp = 0.0365; d = 0.0089; f = 0.0215
C: aug-cc-pVQZ
C1: B + sp = 0.0060; d = 0.0141; f = 0.0291
D: aug-cc-pv5Z
D1: D + sp = 0.00575; d = 0.0147

Table 3
Calculated values of the dipole polarizability of aluminium atom (in a.u.)

Basis set	$\langle\alpha\rangle$
A	51.7
A1	57.3
A2	57.7
A3	57.8
B	58.7
B1	59.3
B2	58.4
B3	58.4
C	58.4
C1	58.4
D	58.0
D1	58.0
Exp.	45.89 \pm 2.02

Experimental value from [4].

of Maroulis [19] for sodium atom, and Das and Thakkar [20] for the second-period atoms. The studies on the importance of the relativistic effects on the dipole polarizability permit to infer that they are negligible for the aluminium atom [21]. The intershell correlation is other effect difficult to include properly in the theoretical calculations. However, it should be less than 1 a.u. according to the calculations of Reinsch and Meyer [6]. Hence, one can estimate a theoretical value between 57.6 and 58.4 with an uncertainty of 1 a.u. This value is far away from the experimental one of 45.89 ± 2.02 a.u. The value was measured with respect to the experimental dipole polarizability of lithium atom reported by Molof et al. [23], which agrees very well with theoretical calculations and, therefore, it is improbable to find the reason of the discrepancy on this point. It seems that a new measurement of the dipole polarizability of aluminium atom would be desirable.

As said before, the value of 45.89 ± 2.02 a.u. has been used to calibrate the experimental measurement of the dipole polarizability of, for instance, silicium [9] and niobium [22] clusters. Assuming a value of 58.0 a.u. to correct the experimental measurements, the dipole polarizability of silicium clusters would augment in almost 20% improving something the concordance with the theoretical calculations. However, for the clusters, the discrepancies are not still well understood.

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