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Reconciliation of the Theoretical and Experimental Value of the Static Electric Polarizability of the Aluminum Atom

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Abstract

The electric polarizability of the aluminum atom has become a benchmark for calibration in electric polarizability measurements of clusters during the past decades. However, there is a large discrepancy between the experimentally measured value and the theoretically predicted one. It is worth to clarify the argument through systematic modern calculations. Here, we present high-level computation of the static dipole polarizability of the ground-state aluminum atom by applying the PC-4 basis set with various ab initio methods including Unrestricted-Hartree–Fock, Møller-Plesset perturbation and the coupled cluster. In contrast to the previously calculated values which deviate from the experimentally measured one by 20%, our recommended value of 47.69 a.u. lies within the experimental one of 46 ± 2 a.u. This reconciliates the theoretical with the experimental value again and reaffirms its reliability as calibration for future experiments.

Keywords Aluminum atom · Electric polarizability · Møller-Plesset perturbation · Coupled cluster theory

Introduction

Being an important property of matter in the fields of physics and chemistry [1–4], the static dipole polarizability plays a crucial role in determining electron-atom scattering, interatomic potentials and optical properties of materials [3, 5], as well as the structures of the clusters [6]. Atomic sodium (Na) or aluminum (Al) is commonly selected as calibration for dipole polarizabilities measurements [7, 8]. Therefore, it is worth obtaining their precise values to the largest extent. For Na atom, several calculated values [9, 10] match well with the experimental ones [8, 11]. In contrast, since the first measurement [12] of Al atom, many reports [13, 14] have questioned its accuracy due to its large discrepancy with calculated values [13–17]. For example, the calculated polarizabilities from CCSD(T) (Coupled Cluster with inclusion of Single and Double excitations and perturbative inclusion of Triple excitations) method with Pople and Dunning basis sets are close to 58, with a deviation of 20% from the experimental value [13]. Lupinetti et al. also obtained the value of about 58 for Al atom by using a modified quadruple-ζ basis set of 21s16p7d6f2g/[13s10p7d6f1g] [14]. However, the latest experimental [8] result reconfirmed the previously measured one explicitly. Therefore, more effort should be applied to revisit the calculations and find out the reason of this inconsistency. To this point, the polarizability of the Al atom was calculated with various methods based on the polarization consistent basis set PC-4 [18, 19]. In order to test the reliability of the basis set for the calculations, the polarizabilities of other atoms with similar electronic configurations as Al were calculated. The results show that d-type functions in the basis set is decisive to the accuracy of the calculated polarizability. Incorrect proportion of d-type functions used in previous studies may be the cause for the large discrepancies. For comparison, the performance of the $6–311++G(3df,3dp)$ [20], aug-cc-pVTZ [21], and the corresponding reformed basis sets are also inspected by calculating the polarizability and ionization potentials of several atoms.

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Computational Details

All calculations were carried out in the Gaussian 09 package [22] using three different basis set configurations: 6–311 + +G(3df,3pd), aug-cc-pVTZ and PC-4 (denoted as A, B, and C). We constructed basis A-, B-, and C-, separately to avoid all d-type functions in basis A, B and C, and added all d-type functions in basis C to basis A- and B- to create basis AC and BC. Here, a more traditional notation is introduced (only for Al atom): basis set A is of the type 14s10p3d1f/[7s6p3d1f], basis set B of the type 42s17p3d2f/[6s5p3d2f], basis C of the type 43s25p6d3f2g1h/[7s6p6d3f2g1h], basis AC of the type 14s10p6d1f/[7s6p6d1f] and basis BC of the type 42s17p6d2f/[6s5p6d2f].

Suitable basis set and theoretical method are the keys to obtain accurate static dipole polarizabilities. Then, the ionization potentials at the CCSD(T) [23–25] level were calculated using basis C to compare with the ones obtained from basis A and B with the same method. Moreover, the reliability of basis set C was verified by calculating the polarizabilities of different aluminum systems—Al^+, Al^{2+}, Al^{3+}, and Al_2—and several atoms adjacent to Al in the Periodic Table.

Basis C with Hartree–Fock and post-Hartree–Fock methods was applied to calculate the static dipole polarizabilities of the Al atom, where all electrons are accounted in order to ensure the intershell correlation effects being considered. Calculations were initiated from the finite-field Unrestricted-Hartree–Fock (UHF) level, and then, Møller-Plesset (MP) perturbation theory and coupled-cluster (CC) calculations were used to further describe electron correlation effects on the polarizabilities with a UHF reference wavefunction. Detailed discussions of the post-Hartree–Fock methods can be found elsewhere [26–28]. The MP perturbation methods used in this work are second-order (MP2), fourth-order (MP4) and partial fourth-order (SDQ-MP4) perturbations. The MP perturbation theory to the energy is written as:

$$E_{MP2} = E_{SCF} + E_{D2}, \tag{1}$$

$$E_{MP3} = E_{MP2} + E_{D3}, \tag{2}$$

$$E_{SDQ-MP4} = E_{MP3} + E_{S4} + E_{D4} + E_{Q4} + E_{R4}, \tag{3}$$

$$E_{MP4} = E_{SDQ-MP4} + E_{T4}, \tag{4}$$

where E_{SCF} is the Hartree–Fock energy; the subscript number n ($n = 2, 3, 4$) is the order; E_{Sn}, E_{Dn}, E_{Tn}, and E_{Qn} represent contributions of energy from single, double, triple, and quadruple substitutions with respect to the reference wavefunction, respectively; E_{R4} is the energy from the renormalization term. The CC methods used in this work are CCSD (Coupled Cluster Singles and Doubles method) and a higher-order version of the CCSD treating triple contributions perturbatively (CCSD(T)). The applications of these high-precision calculation methods in atomic polarizability can be found in previous reports [29, 30].

To unveil the causes of the previous reported inconsistency of calculations with experimental measurements, the polarizability and ionization potential of Al atom via the basis A-, B-, C-, AC, and BC at level of CCSD(T) were performed systematically with the results of MP4 method for reference. The mean polarizability is calculated from the polarizability tensor components as: $\overline{\alpha} = \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right)/3$.

Results and Discussion

The right choice of basis set [28, 31, 32] is crucial to get a reliable calculated polarizability. In order to get insight into their appropriateness, the calculation of ionization potentials will be an unambiguous criterion due to its high sensitivity to the selection of basis sets.

Here, basis sets A, B and C were used to calculate the 1st ionization potentials of aluminum and neighboring atoms in the periodic table. The calculations and experimental values [33] are listed in Table 1 and plotted in Fig. 1 for Li, Be, B, C, Na, Mg, Al and Ga atoms. Basis A, B and C yield discrepancies ranging from 0.24 to 1.47%, 0.35 to 2.68%, and 0.06 to 0.99%, respectively. Interestingly all calculated results underestimated the experimental values. The best agreement in all these atoms was with the value predicted by basis set C (PC-4), which indicates it is the most appropriate.

Furthermore, the ground-state polarizabilities of Al^+, Al^{2+}, Al^{3+}, Al_2 and the neighboring atoms were also computed at CCSD (T) level to test the performance of basis C on predicting polarizability. The results are presented

Table 1 The calculated first ionization potential using different basis sets (in a.u.)

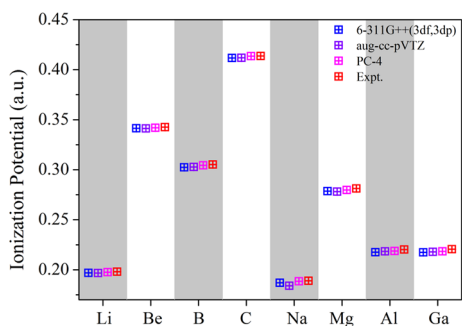| Basis set	Li	Be	B	C	Na	Mg	Al	Ga
A	0.19680	0.34125	0.30231	0.41166	0.18697	0.27856	0.21753	0.21728
B	0.19673	0.34122	0.30256	0.41169	0.18386	0.27800	0.21824	0.21789
C	0.19754	0.34178	0.30431	0.41339	0.18840	0.27971	0.21867	0.21834
Expt.[a]	0.19806	0.34241	0.30508	0.41364	0.18892	0.28109	0.22015	0.22053

[a]Reference [33]

Fig. 1 Comparison of experimental values (Expt., from Ref. [33]) and calculations using three different basis sets

Table 2 The results of the polarizabilities of different Al systems and values previously calculated (Calc.) and measured (Expt.) in the literature are included for comparison

Method	Al^+	Al^{2+}	Al^{3+}	Al_2
This work	24.32	14.43	0.27	125.9
Expt	24.20 (0.75)[d]		0.29[f]	128.2 (13.5)[i]
Calc	24.2[a] [MP4]	14.44[e] [CI]	0.265[g] [SCP]	
	24.14 (0.12)[b] [CI]		0.26[h] [DFT]	
	24.12[c] [CI]			

The digits in parentheses are uncertainties. The letters in the square brackets are the calculated methods, including fourth-order perturbations (MP4), configuration interaction (CI), self-consistent perturbation (SCP), and density functional theory (DFT)

[a]Ref [30]; [b]Ref [34]; [c]Ref [35]; [d]Ref [36]; [e]Ref [37]; [f]Ref [38]; [g]Ref [39]; [h]Ref [40]; [i]Ref [12]

in Table 2 with a comparison to previously calculated and measured values. Our result of Al^+ is 24.32, which is very close to the previously calculated values [30, 34, 35] and tightly lies within the experimental value of 24.20 ± 0.75 obtained by summing oscillator strengths [36]. Although there is no experimental value for Al^{2+} and Al^{3+}, our results of polarizabilities 14.43 and 0.27 agree extremely well with the previously calculated results of 14.44 [37] for Al^{2+} and

0.29 [38], 0.265 [39] and 0.26 [40] for Al^{3+}. For ground-state Al_2 our calculated value is 125.9, which is consistent with the measured value of 128.2 ± 13.5 with the same bond length as previously reported [12, 41].

Next, CCSD (T) level calculation of static dipole polarizabilities was extended to Li, Be, B, C, Na, Mg, and Ga, which are listed in Table 3 and plotted with previously calculated results [9, 10, 16, 17, 42–44, 46–54] and the experimentally measured values [8, 45] in Fig. 2. The values of Li, Na, Mg, and Ga at the CCSD(T) level lie well within the measured values of 164.0 ± 3.4 for Li [45], 161 ± 7.5 for Na [8], 59 ± 16 for Mg [8], and 46.6 ± 4.0 for Ga [8]. Although, there are no experimentally measured polarizabilities available for Be, B and C up to now, our calculated values of 36.43, 20.07 and 11.73 are in accordance with previous calculated values [17, 42, 46, 47]. This confirms the correctness of the basis set and the level of theory selection for the calculation of the Al atom polarizability.

The calculated values of polarizability of Al at UHF and post-Hartree–Fock level are presented in Table 4. All the results by post-Hartree–Fock methods lie within the uncertainty of the experimentally measured value of 46 ± 2 [8], except the value at MP2 level, which is slightly larger. This is probably due to the neglect of the high order perturbation terms. The higher accurate benchmark results at the level of CCSD(T) and MP4 are almost the same, indicating reliability of calculated polarizability of Al.

As listed in Table 4, it is clear that our results have large discrepancies with several calculated values from previous works. To understand these discrepancies, further calculation of the polarizability and 1st ionization potential of Al using CCSD(T) and MP4 methods with basis A-, B-, C-, AC, and BC were conducted, the results are presented in Table 5.

As shown in the Table 5, the results calculated using CCSD(T) are almost identical to those of MP4. The similarity of calculated polarizabilities and ionization potentials using basis A-, B-, C-, indicate that in basis A, B and C, the functions that make the difference are d-type components. Additionally, calculations with basis AC and BC
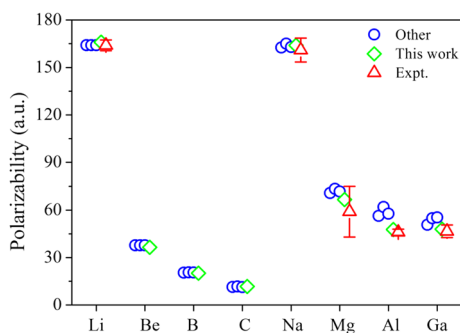
Table 3 Polarizabilities of the atoms adjacent to Al in the periodic table

	Li	Be	B	C	Na	Mg	Ga
This work	166.01	36.43	20.07	11.73	163.96	66.61	47.96
Other	164.05[a]	37.755[a]	20.47[f]	11.39[h]	162.6[k]	70.76[o]	49.9[g]
	164.084[b]	37.74[a]	20.59[g]	11.67[i]	165.06[l]	73.4[p]	51.6[g]
	164. 113[c]	37.73[e]	20.53[g]	11.26[j]	162.88[m]	71.8[q]	54.9[r]
Expt	164.0 (3.4)[d]				161 (7.5)[n]	59 (16)[n]	46.6 (4.0)[n]

The digits in parentheses are uncertainties

[a]Reference [42]; [b]Reference [43]; [c]Reference [44]; [d]Reference [45]; [e]Reference [46]; [f]Reference [47]; [g]Reference [17]; [h]Reference [48]; [i]Reference [49]; [j]Reference [50]; [k]Reference [9]; [l]Reference [10]; [m]Reference [51]; [n]Reference [8]; [o]Reference [52]; [p]Reference [53]; [q]Reference [54]; [r]Ref[16]

Fig. 2 Static electric polarizabilities of atoms Li, Be, B, C, Na, Mg, Al and Ga. Previously calculated values [9, 10, 16, 17, 42–44, 46–54] (open blue circles), measured values [8, 45] (red triangles), and calculated values in this work (green diamonds)

Table 4 Calculated polarizabilities of Al atom at different levels (in a.u.)

Basis set	Method	α
PC-4	HF	50.96
	MP2	48.20
	SDQ-MP4	47.76
	MP4	47.68
	CCSD	47.78
	CCSD(T)	47.69
	PNO-CEPA	56.3[a]
Other	Numerical MCSCF	62.0[b]
	CCSD(T)	57.74[c]
Expt		46 ± 2[d,e]

The methods of the other calculated results include pseudonatural orbital configuration expansion (PNO-CEPA), numerical multi-configuration self-consistent field (MCSCF), fourth-order perturbations (MP4), configuration interaction (CI), and CCSD(T)

[a]Reference [15]; [b]Reference [16]; [c]Reference [14]; [d]Reference [8]; [e]Reference [12]

Table 5 Comparison of the polarizabilities and ionization potentials of Al atom using CCSD(T) and MP4 methods with different basis sets (in a.u.)

Basis set	Polarizability		Ionization potential	
	CCSD(T)	MP4	CCSD(T)	MP4
A	51.7[a]	51.79	0.21753	0.21697
B	58.7[a]	58.69	0.21824	0.21773
C	47.69	47.68	0.21867	0.21811
A-	41.45	40.45	0.19453	0.19467
B-	42.33	42.48	0.19440	0.19454
C-	41.50	40.13	0.19544	0.19563
AC	47.57	47.55	0.21850	0.21798
BC	48.64	48.64	0.21819	0.21762
Expt	46 ± 2[b,c]		0.22015	

[a]Reference [13]; [b]Reference [8]; [c]Reference [12]

Table 6 Comparison of the polarizabilities and ionization potentials of Mg atom using CCSD(T) and MP4 methods with different basis sets (in a.u.)

Basis set	Polarizability		Ionization potential	
	CCSD(T)	MP4	CCSD(T)	MP4
A	72.70	72.59	0.27856	0.27707
B	73.52	73.63	0.27800	0.27636
C	66.61	66.10	0.27971	0.27827
A-	59.09	59.44	0.27582	0.27393
B-	58.78	59.06	0.27618	0.27430
C-	58.85	59.03	0.27631	0.27442
AC	67.42	67.30	0.27891	0.27741
BC	67.29	67.17	0.27913	0.27761
Expt	59 ± 16[a]		0.28109[b]	

[a]Reference [8]; [b]Reference [33]

show improved results of polarizability and 1st ionization potentials with respect to the results with basis A and B, suggesting that the correct inclusion of d-type functions is crucial for the accuracy of the polarizability calculations.

It is worth noting that overestimated values of the polarizability that were reported to match experimental results [55, 56] cannot be used for the judgement of the accuracy of the calculations. In those experiments aluminum atoms were generated by wire explosions that certainly populated the low lying excited states of aluminum, considering they are only 161 K above their ground states [57].

To explore the influence of d-type functions on the calculation of the polarizabilities of other atoms, Mg atom was taken as a testing example. It was found that the calculated polarizability of Mg (66.61) by PC-4 basis set is also significantly smaller than the previously reported value (~71) [30, 53, 54], but is closer to the latest experimental value 59 ± 16 [8]. In order to examine whether it is also due to d-type functions, all of those basis sets used in Al atom have been applied to calculate the polarizability of Mg atom including A, B, C, A-, B-, AC and BC. The calculated results are summarized in Table 6, which shows similar effect as Al atom, the d-type functions significantly affect the polarizability of Mg. After changing the d-type functions for A and B basis sets, the ionization potentials are also closer to the experimental values, suggesting the reliability of the calculated results.

Based on the analysis above, we determine that it is the integration of unsuitable d-type functions in basis A and B that results in incorrect values for the calculated polarizability of Al, indicating the necessity of basis sets re-optimization in previous calculations. In addition to Al atom, d-type functions also strongly influence Mg polarizability calculations.

Conclusion

In summary, updated calculations, at the level of CCSD(T) with a proper basis set, produce a value of 47.69 for the static polarizability of the Al atom (α_{Al}), which is consistent with the accepted experimental result of 46 ± 2. Systematic analysis of the effect of selected basis sets, reveals that the cause of the previous large inconsistency was due to the inappropriate inclusion of d-type functions. It eliminates a decades old discrepancy in atomic physics and reaffirms the correct use of α_{Al} as a benchmark for calibration in polarizability measurements, reconciling theory with experiment again.

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