

Electric quadrupole moments and electron affinities of atoms from H to Cl: a coupled-cluster study

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Abstract

Electric quadrupole moments and electron affinities of ground-state atoms from H to Cl are computed at the infinite-order coupled-cluster method with the noniterative (CCSD(T)) and iterative (CCSDT) inclusion of all single, double, and triple excitations, respectively. Generally, there exists some correlation between the magnitudes of quadrupole moments and electron affinities (A) of the atoms. The highest level of our calculations delivers an accuracy in the computed A values compared to experimental data not worse than 0.03 eV. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

By analogy with the well-known attachment of electrons by systems possessing sufficiently large permanent dipole moments [1], it was suggested [2] that an electron can be attached by the field of a permanent quadrupole moment of a system lacking a permanent dipole moment. Since atoms are exactly such systems, it is interesting to check the correlation between the magnitudes of atomic electron affinities and atomic quadrupole moments.

The electric quadrupole moment is a second-rank tensor defined [3] by the equation

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i (3r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}), \quad (1)$$

where e_i are charges of particles $r_i^2 = x_i^2 + y_i^2 + z_i^2$

(r_i are the particles positions at a coordinate system), $\alpha, \beta = x, y, z$, and δ_{ij} is the substitution tensor (the Kronecker symbol) defined as $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$ and zero otherwise.

Components of the quadrupole moment of a ground-state atom can be defined [4,5] as

$$\langle \Theta_{\alpha\alpha} \rangle = -\frac{1}{2} e \sum_i^Z \langle 0 | 3r_{i\alpha}^2 - r_i^2 | 0 \rangle, \quad (2)$$

because nondiagonal elements vanish by symmetry. Here $\alpha = x, y, z$ and Z is the nuclear charge of an atom. Experimental [6–8] and theoretical [9–11] data on atomic quadrupole moments are rather scarce and concern mainly excited states of atoms whose quadrupole moments are zero by symmetry in the ground states. The only ground-state quadrupole moments appear to have been measured for Al (${}^2P_{3/2}$) and In (${}^2P_{3/2}$) [11].

The aim of the present work is to compute the quadrupole moments and electron affinities (A) of

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atoms from H to Cl at the coupled-cluster level of theory with large basis sets. Also, we have calculated quadrupole moments of atomic singly charged anions at the same level and the atomic A with the Hartree–Fock Density-Functional Theory (HFDFT).

2. Computational details

The calculations have been performed with the ACES II suite of programs [12] at the infinite-order coupled-cluster level of theory with the noniterative (CCSD(T)) [13,14] and iterative (CCSDT) [15] inclusion of all single, double and triple excitations. In the electron affinity calculations, we have used also the HFDFT(B3LYP) approach as implemented in ACES II [16]. Two large basis sets are employed: the atomic natural orbital basis of Widmark–Malmquist–Roos (WMR) (H[8s4p3d/6s4p3d], ..., Cl[17s12p5d4f/7s7p5d4f]) [17], and the largest Woon–Dunning basis, cc-aug-PV5Z (H[9s5p4d3f2g/6s5p4d3f2g], ..., Cl[21s13p5d4f3g2h/8s7p5d4f3g2h]) [18].

Quadrupole moments are calculated at the HF and CCSD(T) levels because, at this point, the relaxed density for the full CCSDT method has not been

implemented. At the HF level, quadrupole moments are calculated as usual [19]:

$$\langle \Theta_{\alpha\alpha} \rangle = \int \Theta_{\alpha\alpha}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} = \text{Tr}(\Theta\rho), \quad (3)$$

where ρ is the HF electronic density. At the CCSD(T) level, we use the so-called “relaxed” density $D(\mathbf{r}) = \sum_{p,q} \psi_p(\mathbf{r}) D_{pq} \psi_q^*(\mathbf{r})$, where D_{pq} consists of the one-particle response density and the MO relaxation part [20,21]. Consequently, Eq. (3) is replaced by the equation

$$\langle \Theta_{\alpha\alpha} \rangle = \int \Theta_{\alpha\alpha}(\mathbf{r}) D(\mathbf{r}) d\mathbf{r} = \sum_{p,q} \Theta_{\alpha\alpha}^{pq} D_{pq}. \quad (4)$$

By definition, the atomic electron affinity is the difference between the total energies of an anion and its neutral parent atom in their ground states.

3. Results and discussion

3.1. Electron affinities

Let us discuss first the accuracy of our computational methods in reproducing the experimental A [22], measured with rather high accuracy. Table 1 compares the experimental data and theoretical A

Table 1

Electron affinities (in eV) of atoms computed at the CCSD(T), CCSDT and HFDFT (B3LYP) levels with the WMR and cc-aug-PV5Z bases together with experimental data

Species	WMR			cc-aug-PV5Z ^a			A_{exp}^b
	B3LYP	CCSD(T)	CCSDT	B3LYP	CCSD(T)	CCSDT	
H	0.802	0.723	0.723	0.815	0.747	0.747	0.754
Li	0.469	0.616	0.616	–	–	–	0.618
Be	–0.228	–0.349	–	–	–	–	< 0
B	0.322	0.242	0.256	0.324	0.257	0.271	0.277
C	1.228	1.232	1.240	1.227	1.252	1.259	1.263
N	–0.572	–0.213	–	–0.486	–0.201	–	< 0
O	1.479	1.355	1.361	1.479	1.428	1.432	1.461
F	3.328	3.326	3.317	3.327	3.406	3.395	3.399
Na	0.472	0.542	0.541	–	–	–	0.548
Mg	–0.561	–0.468	–	–	–	–	< 0
Al	0.344	0.406	0.418	0.358	0.424	0.433	0.441
Si	1.251	1.376	1.381	1.253	1.401	1.405	1.385
P	0.791	0.617	0.625	0.798	0.706	0.714	0.747
S	2.080	1.952	1.952	2.083	2.058	2.059	2.077
Cl	3.579	3.505	3.497	3.582	3.632	3.623	3.617

^a The cc-aug-PV5Z basis was not available for Li, Be, Na and Mg. ^b See Ref. [22]; the A of Al is from Ref. [23].

obtained at the HFDFDFT (B3LYP), CCSD(T), and CCSDT levels with the use of the WMR and cc-aug-PV5Z basis sets. Comparison shows that the CCSD(T) and CCSDT approaches provide rather close values (within the same basis set). The most appreciable improvement with respect to experimental data is obtained for the A of the boron atom, where the iterative inclusion of triples results in a 0.014 eV gain, bringing the theoretical CCSDT/cc-aug-PV5Z A of B very close to the experimental A .

The A computed at the CCSD(T) and CCSDT levels are rather sensitive to the inclusion of higher- l angular harmonics into the basis, which is consistent with the fact that the convergence of the correlation energy in coupled-cluster methods is proportional to $1/L^{-4}$, where L is the highest angular momentum of basis atomic orbitals [19]. This basis dependence would mean also that there seems to be no fortuitous cancellation of the correlation contributions to the total energies of an atom and its anion. The most sensible improvement (up to 0.1 eV) is found for the A of O, F, P, S, and Cl, where an extra electron attaches to half-filled np -shells. As expected [25,26],

the HFDFDFT A are practically independent on the inclusion of harmonics with $l > 3$.

Table 2 presents the total energies of several selected atoms and their anions obtained at all the levels of theory applied in the present work. As is seen, the WMR and cc-aug-PV5Z bases provide rather close values, especially at the HFDFDFT level. At the CCSD(T) and CCSDT levels, the WMR basis provides even slightly lower total energies for the B, Al, and Cl atoms and their anions with respect to those obtained with the cc-aug-PV5Z basis. Therefore, the essential improvement in the A values when going from the WMR basis to the cc-aug-PV5Z basis is almost completely due to a better account of the balance between the correlation energies of an anion and its neutral parent atom when using the cc-aug-PV5Z basis, which includes angular harmonics up to $l = 5$, whereas the highest l in the WMR basis is 3.

The WMR basis set for hydrogen does not contain functions with $l > 2$ and the CCSDT level (which is equivalent to CCSD and full-CI in this case, as well as to full-CI for the Li–Li[−] pair) with this basis

Table 2

Total energies (in Hartree) of atoms computed at the CCSD(T), CCSDT and HFDFDFT(B3LYP) levels with the WMR and cc-aug-PV5Z bases

Species	Method	WMR		cc-aug-PV5Z	
		neutral	anion	neutral	anion
B	CCSDT	−24.632697	−24.642138	−24.630229	−24.640185
	CCSD(T)	−24.632252	−24.641130	−24.629818	−24.639259
	B3LYP	−24.644512	−24.656369	−24.644545	−24.656466
C	CCSDT	−37.819178	−37.864746	−37.819967	−37.866234
	CCSD(T)	−37.818682	−37.863962	−37.819523	−37.865547
	B3LYP	−37.836040	−37.881173	−37.836098	−37.881207
O	CCSDT	−75.033160	−75.083159	−75.037459	−75.090069
	CCSD(T)	−75.032823	−75.082624	−75.037159	−75.089636
	B3LYP	−75.064937	−75.119303	−75.065015	−75.119375
F	CCSDT	−99.690033	−99.811946	−99.700191	−99.824972
	CCSD(T)	−99.689838	−99.812078	−99.700031	−99.825204
	B3LYP	−99.734749	−99.857061	−99.734888	−99.857164
Al	CCSDT	−242.070904	−242.086253	−242.042694	−242.058622
	CCSD(T)	−242.070454	−242.085382	−242.042286	−242.057854
	B3LYP	−242.336727	−242.349385	−242.337054	−242.350214
Cl	CCSDT	−459.848968	−459.977505	−459.815609	−459.948753
	CCSD(T)	−459.848373	−459.977207	−459.815067	−459.948555
	B3LYP	−460.105896	−460.237437	−460.106266	−460.237908

underestimates the A of H by 0.03 eV compared to the “experimental” value of 0.754209(3), which, actually, was calculated by Pekeris [24] in 1958, taking into account hyperfine interactions, and was included in the compilation of experimental values as the most reliable A of the H atom by Hotop and Lineberger [22]. Our CCSDT/cc-aug-PV5Z value of the hydrogen A is smaller only by 0.007 eV than Pekeris’ “exact” value. The HF-DFT hydrogen A is found to be almost the same in both bases.

As is seen from Table 1, the largest deviation of our A values obtained at the CCSDT/cc-aug-PV5Z level from the experimental data is about 0.03 eV. However, effects of higher-order interactions (and relativistic, in particular) can be of the same order of magnitude; therefore, let us compare our CCSDT/cc-aug-PV5Z A with those obtained by a multireference configuration-interaction (MRCI) approach with a large contracted $13s11p6d5f5g5h$ basis for B, C, O, and F [27]. Their values of 0.278, 1.264, 1.454, and 3.363 eV are in nice accord with ours – 0.271, 1.259, 1.432, and 3.395 eV, respectively. It appears that quadrupoles and higher excitations will contribute to the atomic A not more than 0.03 eV with the cc-aug-PV5Z basis, whereas such contributions could be anticipated to be larger in

molecular systems. Thus, for example, the CCSDT/cc-aug-PV5Z A of NH was computed to be smaller by 0.08 eV than the experimental value [28].

3.2. Quadrupole moments

Quadrupole moments of ground-state atoms and their anions computed according to Eq. 3 and Eq. 4 at the HF and CCSD(T) levels, respectively, are presented in Table 3 in atomic units ($1 \text{ au} = ea_0^2 = 1.345035 \cdot 10^{-26} \text{ e.s.u. (or esu} \cdot \text{cm}^2)$). Since the charge distributions are symmetric about z -axis, then all the nondiagonal components $Q_{\alpha\beta}$ do vanish and two diagonal components are equal to each other [3], being of the opposite sign and twice smaller than the third component because of the relationship $Q_{xx} + Q_{yy} + Q_{zz} = 0$.

Experimentally measured atomic quadrupole moments are given [6] by

$$\Theta_{zz} = -\frac{1}{2}e \sum_i \langle J, M_J = J | 3z_i^2 - r_i^2 | J, M_J = J \rangle. \quad (5)$$

Note that the “average” quadrupole moment for any atomic J -multiplet obtained as the sum of the

Table 3

Electric quadrupole moments (in au) of atoms and their anions obtained at the HF and CCSD(T) levels with the cc-aug-PV5Z and/or WMR basis. Zero entry means that the corresponding quantity was computed to be smaller than 10^{-7}

Atom	Basis	HF		CCSD(T)		A_{exp}	Anion	CCSD(T)	
		Θ_{xx}	Θ_{zz}	Θ_{xx}	Θ_{zz}			Θ_{xx}	Θ_{zz}
H	WMR	0.0	0.0	0.0	0.0	0.754	H ⁻	0.0	0.0
Li	WMR	0.0	0.0	0.0	0.0	0.618	Li ⁻	0.0	0.0
Be	WMR	0.0	0.0	0.0	0.0	< 0	Be ⁻	not observed	
B	PV5Z	-2.49	1.25	-2.32	1.16	0.277	B ⁻	-3.15	6.30
C	PV5Z	-0.74	1.48	-0.71	1.41	1.263	C ⁻	0.0	0.0
N	PV5Z	0.0	0.0	0.0	0.0	< 0	N ⁻	not observed	
O	PV5Z	-0.95	0.475	-0.95	0.475	1.461	O ⁻	-0.90	1.79
F	PV5Z	-0.34	0.67	-0.34	0.68	3.399	F ⁻	0.0	0.0
F	WMR	-0.34	0.68	-0.34	0.68		F ⁻	0.0	0.0
Na	WMR	0.0	0.0	0.0	0.0	0.548	Na ⁻	0.0	0.0
Mg	WMR	0.0	0.0	0.0	0.0	< 0	Mg ⁻	not observed	
Al	PV5Z	-5.76	2.88	-5.24	2.62 ^a	0.441	Al ⁻	-5.18	10.36
Al	WMR	-5.88	2.88	-5.22	2.61		Al ⁻	-4.85	9.70
Si	PV5Z	-1.815	3.63	-1.67	3.34	1.385	Si ⁻	0.0	0.0
P	PV5Z	0.0	0.0	0.0	0.0	0.747	P ⁻	-4.96	2.48
S	PV5Z	-2.17	1.085	-2.00	1.00	2.077	S ⁻	-1.44	2.88
Cl	PV5Z	-0.81	1.62	-0.76	1.52	3.617	Cl ⁻	0.0	0.0

^a Experimental value is $+2.53 \pm 0.15$, see Ref. [6].

quadrupole moments of all states with M_J running over permitted values $-J \geq M_J \geq J$ vanishes, since it corresponds to a spherically symmetric electron distribution. Quadrupole moments of atomic S -states are zero as follows from symmetry rules [9], which are valid up to the order of hyperfine interaction effects, estimated for atomic hydrogen to be of the order of 10^{-8} – 10^{-9} au [29]. Since experimentally obtained values of quadrupole moments may be positive [6] or negative [8], depending on a particular state from a given multiplet selected for measurements, we present both positive and negative components of atomic quadrupole moments in Table 3.

As is seen from the table, the atoms and anions possessing spherical symmetry (i.e., having the angular momentum $L = 0$ (S -states)) have zero quadrupole moments, as expected. Actually, the departure from zero in these cases calibrates the numerical accuracy of the calculations, which depends crucially on the basis set used and integral evaluations (the integral threshold in ACES II is 10^{-14}). For example, we have obtained $\Theta_{zz} = 0.94 \cdot 10^{-8}$ for N and $\Theta_{zz} = 0.17 \cdot 10^{-7}$ for Ar.

Our values obtained at the HF and CCSD(T) levels are rather close to each other, which is in agreement with the same magnitude of differences obtained between the values calculated by the HF and finite-element multiconfiguration HF method (MCHF) [10,11,30] as well as with our results for the COS, CO₂, and CS₂ molecules [31].

To see basis-set effects, we have calculated quadrupole moments of F and Al with the WMR and cc-aug-PV5Z basis sets. As shown in the entries of Table 3, no appreciable difference can be observed. Our computed value of the positive quadrupole moment component for Al (2.62 au) is in accord with the experimental value of 2.53 ± 0.15 au [6] to within the experimental error bars. Another theoretical value obtained by Sundholm and Olsen [11] using MCHF gives 2.58 au.

Concerning the correlation between the magnitudes of atomic quadrupole moments and electron affinities, one could observe several trends. First, the atoms with zero quadrupole moments either do not attach an extra electron (He, Be, N, Ar, Mg, and Ar) or have relatively small and similar A values (H, Li, Na, and P). However, the B and Al atoms possess larger quadrupole moments (in fact, Al possesses the

penultimate positive quadrupole moment component), but have the smallest A .

On the other hand, the C⁻ anion has an excited state with a binding energy of 0.033 eV (which arises from the same $2p^3$ -shell as does the ground state), the Al⁻ anion also has an excited state with a binding energy of 0.109 eV ($3p^2$ shell), and the Si⁻ anion possesses two excited states with binding energies of 0.523 and 0.029 eV ($3p^3$ shell), respectively, according to experimental measurements [22]. Correspondingly, C, Al, and Si possess the maximal positive Θ_{zz} components among the $2p$ - and $3p$ -atoms.

The increase in positive components of the quadrupole moments within sub- np -shells is consistent with increasing the atomic A (subseries Be → B → C, N → O → F, Mg → Al → Si, P → S → Cl), which appears to reflect the attachment of an extra electron by a stronger field. On the other hand, one can see that the atoms with the smallest (in absolute value) negative quadrupole moment components possess the largest A (F in the $2p$ -series and Cl in the $3p$ -series). The behavior of the negative components of the quadrupole moments along the series is the same as that of the positive component since they are related as $\Theta_{xx} = -2\Theta_{zz}$. As a curiosity, one could surmise that atoms with zero quadrupole moments should have the largest A if we extrapolate over the series N → O → F and P → S → Cl. However, this is not so because the relative inertness of closed shells enters in force.

Among the anions, only B⁻, O⁻, Al⁻, P⁻, and S⁻ possess non-zero quadrupole moments. One can see that the values of the quadrupole moment components of these anions are inversely proportional to the A magnitudes of the corresponding neutral parents. It appears to be related to the diffuseness of the anion charge distributions, since the extra electron is more loosely bound in the anions corresponding to atoms with smaller A .

4. Conclusion

The results of our study on the electron affinities and electric quadrupole moments of atoms from H to Cl at the infinite-order coupled-cluster method with the noniterative and iterative inclusion of all single,

double, and triple excitations (CCSDT) allow the following conclusions:

1. The electron affinities (A) of atoms are sensitive to the inclusion into basis sets of angular harmonics with $l > 3$.
2. The A obtained at the CCSDT level agrees with experiment within 0.01–0.03 eV, which indicates that higher excitations (quadruples, pentuples, etc.) will provide rather small contributions to the A magnitudes.
3. The atomic electric quadrupole moments (EQM) are frequently rather insensitive to the level of correlation, with corrections varying from 0 to about 10%.
4. Although there is no direct relationship between the magnitudes of the atomic A and EQMs, the behavior of EQMs within the subseries $\text{Be} \rightarrow \text{B} \rightarrow \text{C}, \text{N} \rightarrow \text{O} \rightarrow \text{F}, \text{Mg} \rightarrow \text{Al} \rightarrow \text{Si}, \text{P} \rightarrow \text{S} \rightarrow \text{Cl}$ is consistent with the increase of A in this subseries.
5. The F and Cl atoms possess the largest A in the series but have the smallest negative EQM components among the other $2p$ - and $3p$ -atoms, respectively.

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