"Atomic" Determination of the ^{23}Na, ^{25}Mg, and ^{27}Al Nuclear Quadrupole Moments: How Accurate Are the "Muonic" Values?

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The quadrupole moments of ^{23}Na and ^{27}Al are determined by combining the calculated electric-field gradients of Na($3p;^2P^\circ$) and Al($3p;^2P^\circ$) with experimental quadrupole coupling constants. $Q(^{25}\mathrm{Mg})$ was determined previously using the same method [Nucl. Phys. **A534**, 360 (1991)]. Contrary to $Q(^{25}\mathrm{Mg})$ the "atomic" values for $Q(^{23}\mathrm{Na})$ and $Q(^{27}\mathrm{Al})$ lie outside the error limits of the "muonic" values. The obtained values for $Q(^{23}\mathrm{Na})$, $Q(^{25}\mathrm{Mg})$, and $Q(^{27}\mathrm{Al})$ are 0.1089(32), 0.1994(20), and 0.1402(10) b, respectively, as compared to the muonic values of 0.1006(20), 0.201(3), and 0.150(6) b.

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A nuclear quadrupole moment Q can be obtained from the experimental quadrupole coupling constants, eqQ/h or B, combined with an estimate of the electric-field gradient at the nucleus, q. An early method was to obtain q from the $\langle r^{-3}\rangle$ values in magnetic hyperfine coupling and to introduce Sternheimer corrections [1] to account for quadrupole shielding. Alternatively, q can be obtained from high-quality *ab initio* calculations on atomic or molecular systems without any further correction factors. The relation between q (in atomic units, a.u.), Q (in barns, 1 b $=10^{-28}$ m^2), and the quadrupole coupling constant eqQ/h (in MHz) is

$$Q=-(eqQ/h)/234.9647q\,. \qquad (1)$$

In this work the quadrupole moments are deduced from the experimental eqQ/h using accurate multiconfiguration Hartree-Fock values for q. Previously, the quadrupole moments of ^{9}Be [2], ^{10}B [3], ^{11}B [3], ^{11}C [4], ^{14}N [5], ^{17}O [4], ^{21}Ne [4], ^{27}Mg [6], ^{33}S [7], and ^{35}S [7] have been determined using the same methods.

Nuclear-model-independent quadrupole moments can also be provided by mesonic x-ray experiments [8]. The quadrupole moments of ^{23}Na [9], ^{25}Mg [10], and ^{27}Al [10,11] have been obtained from the hyperfine splittings of the muonic atoms, i.e., atoms where one electron is replaced by a muon. In muonic atoms, the muon moves almost independently of the electrons and penetrates the nucleus only slightly. The orbits of the muon are almost hydrogenlike, and the electric-field gradient of the muon can be obtained by solving the Dirac equation for the muon. However, small corrections must be made for nuclear finite-size effects, vacuum polarization, nuclear polarization, and magnetic hyperfine structure [8-11]. The nuclear finite-size (penetration) effect which is the largest of these corrections changes the estimate of the quadrupole moments of ^{23}Na, ^{25}Mg, and ^{27}Al by about 1.0%-1.5% [9,10]. However, the main source of uncertainty of the muonic-experiment values is statistical error. The free parameters in the fit to the experimental spectra were the height of the background, the quadrupole moment, and the position and the absolute intensity of the x-ray line [8-11].

Nuclear scattering experiments [12-17] have also been used to obtain values for quadrupole moments. The uncertainty of the values obtained from a scattering experiment is at least 10%. One exception is the quadrupole moment of ^{7}Li which has recently been determined from nuclear scattering data with an accuracy of 1.5% [17].

Nuclear theory calculations also provide values for quadrupole moments, the accuracy of which is about 10%-20% [18-23].

The purpose of this work is to calculate the electric-field gradients of Na($3p;^2P_{3/2}$) and Al($3s^23p;^2P_{3/2}$) with an uncertainty less than 1%, and to deduce accurate quadrupole moments of ^{23}Na and ^{27}Al from them and experimental data. This method is completely independent of that of the muonic measurement. The confidence of the muonic experiments can therefore be checked by comparing the "atomic" values for $Q(^{23}\mathrm{Na})$, $Q(^{27}\mathrm{Al})$, and $Q(^{25}\mathrm{Mg})$ [6] with the corresponding "muonic" results.

The finite-element multiconfiguration Hartree-Fock (MCHF) method used in this work has previously been discussed in Refs. [2-7,24,25]. To facilitate the selection of the configurations, the MCHF method is based on the restricted active space (RAS) [26,27] method. The RAS method is a generalization of the complete active space (CAS) method [28]. In the RAS method, the active orbital space consists of three subspaces, the RAS I, the RAS II, and the RAS III. In a RAS calculation a lower limit is given for the number of electrons in RAS I, and an upper limit is given for the number of electrons in RAS III, while no restriction is put on the number of electrons in RAS II. The following notations are used for the RAS calculations: inactive orbitals//the orbitals of RAS I {minimum number of electrons in RAS I}/the orbitals of RAS II/the orbitals of RAS III (maximum number of electrons in RAS III). When a minus sign appears in the notation it means that all the orbitals to the left of the minus sign are frozen, while those to the right of the minus sign are fully energy optimized. The number of local basis functions (grid points) per symmetry is

201 resulting in a basis-set truncation error in the electric-field gradient of less than 10^{-4} a.u.

Sodium.—The multireference, all singles and doubles (MR-SD), *sp* and *spd* limits for q of $\mathrm{Na}(^2P)$ are obtained as follows: The slight polarization of $2p$ caused by the $3p$ electron is difficult to describe with fully energy-optimized shells, so the Hartree-Fock (HF) shells are augmented by a polarization p shell. In the optimization of the polarization p shell ($2p^*$), the HF shells are frozen while $2p^*$ is optimized and only single excitations are allowed from $2s$ and $2p$ to $3p$ and $2p^*$. In the subsequent calculations, the HF shells and $2p^*$ are frozen. The active set of shells is systematically augmented by energy optimized s, p, and d shells until the change in q becomes small enough to be neglected. We did not find it necessary to construct polarization shells of s and d symmetry, while a polarization shell of f symmetry significantly improved the convergence of q with respect to the number of f shells. The largest MR-SD RAS calculation in the *spd* basis [$1s//1s1p\{6\}/1p/1p-5s4p5d(2)$] yielded a q of -0.1069 a.u., while the corresponding MR-SD configuration interaction (CI) calculation in the same *sp* shells [$1s//1s1p\{6\}/1p/5s5p-(2)$] yielded a q of -0.1084 a.u. In the *sp* basis triple excitations from $2s$ and $2p$ increased q, in absolute value, to -0.1101 a.u. which is also the *sp* limit since quadruple and higher excitations from $2s$ and $2p$ did not significantly change q. Triple excitations to d shells contribute -0.0015 a.u. and the *spd* limit becomes -0.1102 a.u.

In order to reduce the number of f shells needed for estimating the f-shell contribution to q, a polarization f shell was constructed and added to the active set of shells. The polarization f shell was obtained from a $2s//1p\{5\}/1p/3s4p3d-1f(2)$ RAS calculation. The final f-shell contribution of 0.0021 a.u. was estimated as the difference between the $2s//1p\{4\}/1p/3s4p3d-(2)$ CI calculation and the $2s//1p\{4\}/1p/3s4p3d2f-1f(2)$ RAS calculation. The g-shell contribution to q became 0.0003 a.u. and the contributions from higher symmetries are probably smaller and neglected. The relativistic correction to q of -0.0005 a.u. is estimated from a quasirelativistic CI calculation. This value is in agreement with literature values [29,30]. In the quasirelativistic calculation the Darwin and the mass-velocity integrals are added to the one-electron integrals and a CI is performed with modified integrals. In all Na calculations $1s$ is inactive.

Aluminum.—The valence limit for the q of $\mathrm{Al}(^2P)$ of -0.4147 a.u. is calculated in a $2s1p\{10\}/4s4p3d2f$ set of energy-optimized shells. The $3p$ electron will polarize the $1s^22s^22p^6$ core. In the core-correlation calculations, the $2p$ is correlated, while $1s$ and $2s$ are inactive. The *sp* limit of -0.5331 a.u. is obtained by adding the contribution from higher excitations of -0.0010 a.u. to the $2s//1s2p/6s6p-(2)$ CI calculation. The $1s2s2p3s3p$ shells are the most occupied shells of the $2s//2s3p$ CAS calculation. The four first RAS III shells of both s and p symmetry are obtained in a $2s//1s2p/-4s4p(2)$ RAS calculation, and the remaining *sp* shells of the $2s//1s2p/6s6p-(2)$ CI calculation are the energy-optimized s and p shells of the $2s//1p\{4\}/1s1p/4s4p-2s2p(2)$ RAS calculation. The contribution from higher excitations is the difference between the electric-field gradients obtained in the $2s//2s3p$ CAS and the $2s//1s2p/-1s1p(2)$ RAS calculations, respectively. The d-shell contribution to q is the difference between the ones obtained in the $2s//1s2p/-4s4p(2)$ and the $2s//1p\{4\}/1s1p/4s4p3d-1d(2)$ RAS calculations. The correction for higher excitations due to the smaller reference space of the d-shell calculation is only 0.0002 a.u. The fifth d shell contributes 0.0012 a.u. to q, and the final d-shell contribution becomes -0.0365 a.u. The f-shell contribution of -0.0024 a.u. is estimated from the valence calculations. The contribution from higher symmetries is less than the f-shell contribution and may be neglected. To estimate the contribution from $1s$ and $2s$, core-valence calculations are performed. In the core-valence calculations only single excitations are allowed from the core orbitals. The core-valence orbitals of the RAS III space are optimized, while the core and the valence orbitals are frozen. The core-valence correlation correction to q of 0.0010 a.u. is the difference between the ones obtained in the $2s\{3\}/1s1p/4s5p2d-1s1p1d(2)$ and in the $2s//1s1p/4s5p2d-(2)$ calculations. The relativistic correction to q of -0.0015 a.u. is obtained from a quasirelativistic CI calculation in the $2s//1s2p/4s4p2d-(2)$ shells. The calculations are summarized in Table I.

The atomic determinations of nuclear quadrupole moments rely on the measurement of the nuclear quadrupole coupling constants. For Al and Mg, the experimental eqQ/h are accurate, and the error bars of the quadrupole moments are due only to computational uncertainties. There are many measurements of the quadrupole coupling constant (eqQ/h) for $^{23}\mathrm{Na}(3p;^2P_{3/2})$. These experiments have been reviewed by Arimondo, Inguscio, and

TABLE I. The limits of the electric-field gradients at the nuclei of $\mathrm{Na}(3p;^2P)$, $\mathrm{Mg}(3s3p;^3P)$, and $\mathrm{Al}(3p;^2P)$ (in a.u.).

Limit	q(Na)	q(Mg) [a]	q(Al)
Hartree-Fock	-0.0677	-0.2429	-0.4353
sp limit [b]	-0.1101	-0.3355	-0.5331
spd limit [b]	-0.1102	-0.3402	-0.5696
NR limit [b]	-0.1078	-0.3402	-0.5720
C-V corrected [c]	$\cdots$	-0.3402	-0.5710
Rel. corrected [d]	$-0.1083(9)$	$-0.3417(34)$	$-0.5738(40)$

[a] Reference [6].

[b] For Na the contribution from the $1s^2$ core is neglected. For Mg, the core-core and core-valence corrections are included in the *sp* limit. For Al, $1s^22s^2$ is the core.

[c] Core-valence correlation corrected values (see footnote b).

[d] Final result. The relativistic corrections are estimated from quasirelativistic CI calculations (see text).

TABLE II. The quadrupole moments of ^{23}Na, ^{25}Mg, and ^{27}Al (in mb) compared to values from the literature. (PW stands for present work.)

Method[a]	$Q(^{23}\text{Na})$	$Q(^{25}\text{Mg})$	$Q(^{27}\text{Al})$	Refs.
hfs+HF calc.	174.1	280.5	184.9	PW,6,PW
hfs+MCHF calc.[b]	108.9(32)	199.4(20)	140.3(10)	PW,6,PW
hfs+atomic calc.	106[c]	200(10)	165(2)	29,37,38
hfs	128(9)	220	149(2)	39,40,41
hfs+Sternheimer	103	···	140(2)	39,. . . ,42
Muonic experiment	100.6(20)	201(3)	150(6)	9,10,10
Nuclear scattering	101(7)[d]	196(4)[d]	155(3)[d]	15,15,15
Nuclear theory	103.4	186.9	134	19,19,18
Nuclear theory	115	206[d]	150.8	18,20,19
Nuclear theory	102.4	235[d]	138.9	23,20,23

[a] hfs stands for hyperfine structure. The quadrupole coupling constants are 2.77(6) MHz [32], 16.009(5) MHz [40], and 18.91526(70) MHz [43,44] for Na(^2P), Mg(^3P), and Al(^2P), respectively.

[b] The error bars include both the experimental and the computational uncertainties.

[c] Obtained using the *eqQ/h* of Ref. [32] and *q* of Ref. [29].

[d] In the adiabatic approximation and assuming an axial charge distribution of the nucleus.

Violino [31]. Based on the experimental results, they estimated an averaged value for the *eqQ/h* of 2.90(21) MHz. The same year Krist *et al.* [32] measured, using the zero-field quantum beat method, an *eqQ/h* of 2.77(6) MHz which is, according to the authors, probably the most accurate value.

From the computational point of view, it is much easier to calculate *q* with the same relative accuracy for core-excited states such as $2p^53s3p$ (^4D) or $2p^53s3d$ (^4F) than for valence states. Experimental determinations of the *eqQ/h* for these core-excited states or corresponding $2p^5$ states of Na$^+$ would therefore be very desirable. Similar measurements have already been performed on potassium [33]. There are also high-quality *ab initio* calculations for *q* on NaH [34], but no spectroscopic data. Accurate *eqQ/h* for the NaF [35] and NaCl [36] molecules exist but the high-quality calculations remain to be done.

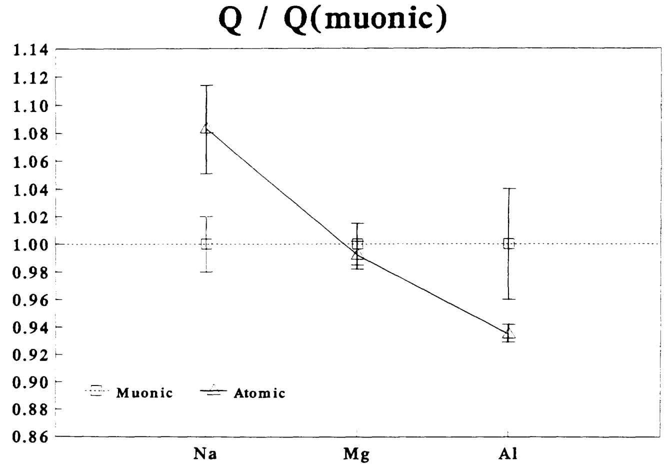

FIG. 1. "Atomic" Q values for nuclei ^{23}Na, ^{25}Mg, and ^{27}Al expressed in terms of the "muonic" Q values.

In Table II, the present values for the quadrupole moments of ^{23}Na, ^{25}Mg, and ^{27}Al are compared to those from the literature. The details of the Mg calculations are reported in Ref. [6]. The electric-field gradient of Na(^2P) has been calculated by several authors [29,45–47]. By combining them with the *eqQ/h* of Krist *et al.* [32], the values for $Q(^{23}\text{Na})$ become 109.7 [45], 108.5 [46], 105.4 [46], 99.3 [47], and 105.9 mb [29], respectively. For Mg, the calculation by Bauche, Couarraze, and Labarthe [37] yields the same $Q(^{25}\text{Mg})$ as the MCHF calculation of Ref. [6] and as the muonic experiment, but with larger error bars. For Al, the previous calculation by Rodgers, Roy, and Das [38] provides a $Q(^{27}\text{Al})$ which is 18% too large compared to the present MCHF value. The $Q(^{23}\text{Na})$ value obtained from the hyperfine structure and adjusted for quadrupole shielding using Sterheimer factors [39] agrees well with the muonic value, while the corresponding result for $Q(^{27}\text{Al})$ [42] agrees with the present MCHF result.

The present $Q(^{23}\text{Na})$ is about 8% larger than the muonic value, the present $Q(^{27}\text{Al})$ is 7% smaller than that of the muonic experiment, while the atomic and the muonic values for $Q(^{25}\text{Mg})$ agree within their stated uncertainties (see Fig. 1). We can therefore not avoid the conclusion that the uncertainty of the muonic x-ray transition experiments may be larger than expected.

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