

Nuclear quadrupole moments from molecular microwave data: The quadrupole moment of ^{85}Rb and ^{87}Rb nuclei and survey of molecular data for alkali-metal nuclei

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The “molecular” values of the quadrupole moment of the Rb and Na nuclei have been obtained by using spectroscopic values of nuclear coupling constants and high-level-correlated relativistic calculations of the electric-field gradients in fluorides and chlorides. The recommended value for the ^{85}Rb nucleus which follows from the present study is about 276 mb, with expected error bars of the order of about 1 mb. This value agrees with the atomic spectroscopy data, and suggests that the quadrupole coupling constant measured for the RbCl molecule is in error. The present calculations for ^{23}Na confirm the earlier molecular result for its electric quadrupole moment, and combined with recent atomic calculations lead to the recommended value in the range 104–105 mb. The molecular results for nuclear quadrupole moments of the alkali-metal nuclei are reviewed leading to a list of the corresponding recommended values. [S1050-2947(99)07510-1]

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I. INTRODUCTION

Among a variety of sources of nuclear quadrupole moment data, nuclear scattering experiments and theoretical models of nuclei do not seem to be particularly reliable [1,2]. Traditionally most of these data follow from measurements of hyperfine splittings in atomic spectra [1,3], and their accuracy can be strongly affected by the precision of measurements [3]. With increasing accuracy of molecular calculations yet another source becomes accessible. This alternative source of accurate values of the electric quadrupole moments of nuclei is given by the microwave spectra of molecules [4,5].

The nuclear quadrupole coupling constants ν_Q^X [4,5] due to a quadrupolar nucleus X can be determined with high accuracy from splittings in rotational spectra in molecules. Although a fitting procedure is involved [5], the derived values of ν_Q^X usually surpass the corresponding atomic data [3] in their accuracy. The determination of the nuclear electric quadrupole moment $Q(X)$ from molecular data for ν_Q^X requires, however, knowledge of the accurate value of the electric-field gradient at X [4,5], and for decades this was the major obstacle. For this reason early attempts to derive nuclear quadrupole moments from the measured values of ν_Q^X were only partly successful [6]. Developments in computational methods of quantum chemistry have made feasible the calculation of molecular electric-field gradients of sufficiently high accuracy, and the nuclear quadrupole coupling constants became a highly competitive source of reliable data for nuclear quadrupole moments [2,7–9]. One should remark that the most accurate value of the electric quadrupole moment of the ^7Li nucleus which is already accepted in

nuclear physics [10] has been derived from microwave spectra of LiH, LiF, and LiCl and accurately calculated electric-field gradients at Li [7,8].

The determination of nuclear quadrupole moments from molecular microwave data is based on the relation between the nuclear quadrupole coupling constant and the electric quadrupole moment of the nucleus. In the case of a linear molecule in the vibrational state ν and with a single quadrupolar nucleus X , the corresponding equation reads:

$$\nu_Q^X(\nu) = e q^X(\nu) Q(X), \quad (1)$$

where q^X is the axial (zz) component of the total electric-field gradient at the nucleus X . Thus the “molecular” values of the nuclear quadrupole moment of X follow from

$$Q(X) = \frac{\nu_Q^X(\nu)}{234.9647 q^X(\nu)}, \quad (2)$$

where $q^X(\nu)$ is assumed to be in atomic units of the electric-field gradient, and the frequency $\nu_Q^X(\nu)$ is measured in MHz. The resulting value of $Q(X)$ is then given in b ($1 b = 10^{-28} \text{m}^2$). Since the quadrupole coupling constants are frequently known with relatively high accuracy (usually better than 0.1%) the main attention is focused on an accurate enough calculation of q^X . This makes the spectroscopic data for diatomic molecules of obvious preference.

In this study the molecular approach is used for the determination of the nuclear quadrupole moment of the ^{85}Rb and ^{87}Rb . There are several values of $Q(^{85}\text{Rb})$ available from atomic measurements. The measurements on the $(5p^1, ^2P_{3/2})$ state [11] gave, with the Sternheimer correction [12] and spin-orbit perturbation, the value of 275 ± 2 mb. A similar measurement on the $(6p^1, ^2P_{3/2})$ state resulted, with the same set of corrections, in the value of 273 ± 2 mb [11]. The same authors derived the $Q(^{85}\text{Rb})$ values from the data for

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the ($7p^1, ^2P_{3/2}$) and ($8p^1, ^2P_{3/2}$) of the Rb atom as equal to 272 ± 6 and 270 ± 17 mb, respectively [11]. Hence the atomic values cover the range from about 253 to 287 mb, with preference given to the results obtained from measurements on low-lying excited states [3]. The data for the excited states ($5p^1, ^2P_{3/2}$), ($6p^1, ^2P_{3/2}$), ($7p^1, ^2P_{3/2}$), and ($8p^1, ^2P_{3/2}$) for ^{87}Rb gave a value of $Q(^{87}\text{Rb})$ equal to 132 ± 9 mb [8,13].

As a matter of fact the error bars of the atomic data are difficult to establish. They should combine both the inaccuracies in the determination of the A and B constants from the atomic spectra [3] and the effect of the use of the Sternheimer correction factor [12]. For instance, the $Q(^{87}\text{Rb})$ value determined from the data for the ($8p^1, ^2P_{3/2}$) state is believed to carry an error of about ± 9 mb [13]. Although the Sternheimer correction factor works extremely well, its value originates essentially from the one-electron theory of many-electron atoms and is subject to some criticism [3]. Similar comments apply to other corrections which are commonly used to derive the nuclear quadrupole moments from atomic hyperfine splittings [3]. In particular, for heavy atoms one should rather carefully consider the contribution due to relativistic effects [3].

The commonly accepted (recommended) ‘‘atomic’’ values of $Q(^{85}\text{Rb})$ [10] are that of Feiertag and zu Pulitz (274 ± 2 mb) [11] and the one derived by Sternheimer and Peierls (263 ± 2 mb) [12,14]. For the ^{87}Rb isotope Feiertag and zu Pulitz [11] give its nuclear quadrupole moment as equal to 132 ± 1 mb. The quoted error bars, though quite narrow, seem to be partly based on the belief in high accuracy of the Sternheimer-Peierls correction scheme. As commented upon by Feiertag and zu Pulitz [11], the reported inaccuracies do not include the uncertainty of the theoretical data (estimated at the level of about 10% [11]). There are also more recent values of $Q(^{85}\text{Rb})$ and $Q(^{87}\text{Rb})$ determined in laser-induced optical pumping of a thermal atomic beam with magnetic state selection [10]. However, their accuracy (228 ± 43 and 130 ± 21 mb, respectively) is rather low. There seem to be neither direct nuclear scattering nor muonic experimental data available for either of the two isotopes of rubidium. One should also mention that the ratio $Q(^{85}\text{Rb})/Q(^{87}\text{Rb})$ has been independently determined from molecular microwave spectra [2.0669 (Ref. [15])], and can be used to check the correctness of independently determined atomic data for the two isotopes.

In comparison with the atomic hyperfine splitting data the nuclear quadrupole coupling constants in $^{85}\text{Rb}^{19}\text{F}$ and $^{87}\text{Rb}^{19}\text{F}$ are known with a very high accuracy; the error bars amount to only a few kHz as compared to the value of ν_Q^{Rb} , which is of the order of several tens MHz [16]. The results of Zorn *et al.* [16] agree very well with earlier data, and their high accuracy appears to be impeccable. Among the relatively light diatomic molecules there is also a rather old measurement of ν_Q^{Rb} in RbCl [17]. Although the quoted accuracy of the coupling constant is not much worse than that in RbF , these data seem to be much less reliable. The results for RbLi [18] would be very useful in the molecular determination of $Q(\text{Rb})$. However, the quadrupole coupling constant for this molecule has been derived under several additional assumptions, and its accuracy is not sufficiently high for the purpose of comparison and/or improving upon atomic values of

$Q(\text{Rb})$. The heavier systems like RbBr and RbI , for which the values of ν_Q^{Rb} are available [5], would certainly pose some computational problems in the determination of accurate values of the electric-field gradient at Rb, and for this reason are dismissed in this study as the possible molecular sources of $Q(\text{Rb})$.

In the present paper the main attention will be therefore focused on the RbF molecule. The methods used to compute the electric-field gradient at Rb are briefly surveyed in Sec. II, and accompanied by the essential computational details of our calculations. The field gradient values obtained for RbF and RbCl will be presented in Sec. III, and used to derive the molecular results for nuclear quadrupole moments of ^{85}Rb and ^{87}Rb . The present study completes a series of earlier determinations of nuclear quadrupole moments of the alkali metal nuclei [7,8,19–21]. It was therefore of interest to survey and compare them with atomic and other results. Such a comparison is presented and discussed in Sec. IV. For the sake of full compatibility with the present results for Rb and recent data [20] for K and in order to remove the possible ambiguities we have also repeated some of our earlier molecular calculations of the ^{23}Na quadrupole moment [19].

II. METHODS AND COMPUTATIONAL DETAILS

A. Computational methods

The computational methods employed in this paper for the calculation of the electric-field gradient at Rb in RbF and RbCl are essentially the same as those used in our earlier studies of other systems [8,19,20,22]. The main part of the electronic contribution is calculated in the one-electron approximation with the self-consistent field Hartree-Fock (SCF HF) method, and then corrected for the electron correlation contribution by using different many-body methods. The lowest level of theory corresponds to the second-order many-body perturbation theory (MBPT2) scheme [23] and is followed by calculations at the level of the coupled cluster (CC) method [23,24]. The CC calculations are limited to the approach with the fully iterative evaluation of the one- and two-body amplitudes (CCSD [23,24]) and corrected perturbatively for the effect of three-body terms (CCSD(T) [24–26]). In the case of systems whose ground electronic state is far away from all other electronic states of the system, the latter approach is known to give excellent account of the electron correlation contribution to energies and properties of molecules [24,26]. The CCSD(T) method has also been successfully used in our earlier calculations of electric-field gradients in different diatomic molecules.

The rubidium atom has high enough nuclear charge that one may expect that the relativistic contributions to properties of RbF and RbCl may be of some importance [27–30]. Since the two molecules have a closed shell structure with full quenching of the angular momentum, the spin-orbit effects should be negligible. The dominant relativistic contribution should follow from the so-called scalar terms, and can be accounted for in quasirelativistic one-component approximations. For relatively light nuclei including the terms of the Pauli approximation [31,32] gives quite satisfactory results [28]. Much more powerful is the one-component Douglas-Kroll (DK) [33] approximation, which has been made into a routine approximation in relativistic quantum chemistry by

Hess [34]. At variance with the Pauli Hamiltonian, the DK energy operator does not involve strongly singular operators and appears to possess some variational stability. When the DK transformation [33–35] is restricted to one-electron terms, the one-component DK calculations affect only the SCF HF code. It is therefore of great advantage that all correlated level calculations can be carried out with exactly the same codes as in the nonrelativistic case. Moreover, the relativistic DK results can be directly compared with the corresponding nonrelativistic (NR) data.

The methods used in this study to obtain the electron correlation contribution to electric-field gradients are nonvariational, and in particular they do not satisfy the Hellmann-Feynman theorem. Hence these contributions need to be calculated as the corresponding energy derivatives with respect to the perturbation strength parameter for the system perturbed by the electric-field gradient operator [36]. In nonrelativistic calculations reported in this paper we have used a finite field perturbation scheme, i.e., the electron correlation energies were calculated in the presence of the electric-field gradient perturbation with its strength scaled by a numerical parameter [28]. Then the electron correlation corrections to the electric-field gradient were evaluated as finite-difference approximations to the first-order derivatives of energies with respect to that parameter [28,37]. An alternative way of computing these corrections is based on the point-charge nuclear quadrupole (PCNQ) model proposed in Ref. [9] and explored in our recent paper [30]. In the nonrelativistic case the two methods give (within the limits of the numerical differentiation scheme) the same results. However, there is certain preference of the point-charge nuclear quadrupole moment model in the case of the relativistic approach.

One of the problems which occur in the case of DK calculations is that the generation of the DK Hamiltonian involves the so-called change of picture [31,38] which needs to be taken into account when calculating the expectation value of the electric-field gradient operator. Hence, the legitimate way of computing either the DK SCF HF electric-field gradient or the DK electron correlation corrections to it should use the form of this operator transformed to the picture which corresponds to the one-component DK Hamiltonian [38]. A convenient way to avoid the change of picture for the field gradient operator follows from the use of the PCNQ model. The small nuclear quadrupole is generated by a set of point charges in the nearest vicinity of the nucleus under consideration. In terms of the DK Hamiltonian, this introduces additional terms in the potential energy operator which is fully transformed to the new picture [30,38]. The calculated energies become functions of the numerical value of the nuclear quadrupole generated in such a way and their derivatives with respect to its value are the expectation values of the electric-field gradient with the change of picture automatically taken into account [30]. The difference between the direct calculation of the expectation value of the (nontransformed) field gradient operator and the value which accounts for the picture change grows very fast with the charge of the nucleus [30].

Finally, let us mention that in most cases the experimental values of ν_Q^X are reported for certain vibrational levels rather than for the equilibrium molecular geometry. Hence the values of the electric-field gradient need to be vibrationally and

rotationally averaged. To obtain the vibrational correction to the electric-field gradient computed at the (experimental) equilibrium geometry, we have used the approximate formula of Buckingham [39] which relates this correction to the shape of the electric-field gradient function, i.e., to its bond distance (R) dependence and to spectroscopic parameters

$$q^X(\nu) = q_e^X + q_{\text{vib}}^X \approx q_e^X + q_1^X(\nu + \frac{1}{2}), \quad (3)$$

where $q_e^X = q^X(R_e)$ and

$$q_1^X = \frac{B_e}{\omega_e} \left[3 \left(1 + \frac{\alpha_e \omega_e}{6B_e^2} \right) \left(\frac{\partial q^X}{\partial \xi} \right)_{\xi=0} + \left(\frac{\partial^2 q^X}{\partial \xi^2} \right)_{\xi=0} \right]. \quad (4)$$

The symbols ω_e , B_e , and α_e denote the usual spectroscopic constants [40] in cm^{-1} , and $\xi = (R - R_e)/R_e$. The calculation of derivatives entering Eq. (4) has been carried out by using the finite-difference approach. Moreover, for the purpose of computing these derivatives the $q^X(R)$ values have been calculated at the level of the DK MBPT2 method. The inaccuracies resulting from the use of the MBPT2 approach are negligible in comparison with other factors and the overall accuracy of the computed values of q^X .

B. Details of numerical calculations

All calculations have been carried out in the algebraic approximation with one electron wave functions expanded into atom-centered sets of Gaussian-type orbitals (GTO's). They have been generated starting from the atom optimized sets of Huzinaga and Klobukowski [41]. The Rb basis set used in the majority of the present calculations has been developed from the (22s14p9d) set of Ref. [41] based on 22 optimized GTO exponents (ζ). This initial set has been extended by one diffuse s -type function ($\zeta = 0.006\,615\,01$), one diffuse p -type function ($\zeta = 0.084\,473\,28$), one diffuse d -type function ($\zeta = 0.348\,364\,25$), a set of six f -type functions ($\zeta = 19.046\,201$, $8.813\,531\,2$, $4.087\,032\,1$, $1.904\,742\,5$, $0.818\,205\,84$, and $0.348\,364\,25$), and a set of two g -type GTO's ($\zeta = 8.813\,531\,2$, and $4.087\,032\,1$). The orbital exponent for the added s function has been obtained from the assumption of the geometric progression in the initial set of exponents. For the other functions the selected orbital exponents are taken from the initial set. The additional functions either make the initial set more diffuse and flexible, or they are chosen from the point of view of the maximum gain in the correlation energy and electric-field-gradient-induced polarization of the density distribution. The derived basis set of the form (23s15p10d6f2g) has been used in its fully uncontracted form. The effect of its further extension in the valence region has also been studied, and will be discussed in Sec. III.

The atomic basis sets for F and Cl are the same as those used in our earlier calculations on KF and KCl [20]. In both cases they follow from the extension of the corresponding atomic sets of Huzinaga and Klobukowski and partial contraction (GTO/CGTO sets). Contractions have been mainly used in the inner core region which is irrelevant for calculations of the electric field gradient at Rb. In the valence region both the F ([15s11p4d/7s7p2d]) and Cl ([18s14p6d/10s8p3d]) GTO/CGTO sets are completely

uncontracted and offer sufficient flexibility for the proper description of the polarization of the density distribution in RbF and RbCl. In order to verify the flexibility of the contracted Cl basis set, we have also carried out some calculations with its fully uncontracted counterpart.

The complementary calculations for NaF and NaCl have been carried out with a fully uncontracted basis set of Na generated in a similar way as that for Rb. The initial (17s10p) GTO set of Huzinaga and Klobukowski has been extended to (18s11p6d4f) by adding one diffuse *s*-type function ($\zeta=0.009\,079\,5$), one diffuse *p*-type function ($\zeta=0.113\,064\,50$), a set of six *d*-type functions ($\zeta=20.068\,482$, $8.484\,485\,0$, $3.584\,967\,5$, $1.513\,629\,3$, $0.639\,997\,38$, and $0.259\,116\,91$), and a set of four *f*-type functions ($\zeta=8.484\,485\,0$, $3.584\,967\,5$, $1.513\,629\,3$, and $0.639\,997\,38$). This GTO set is different from the one used in earlier calculations of q^{Na} in NaF and NaCl [19]. However, this set is fully compatible with that of the rubidium atom and with the GTO set used for potassium [20].

In NR CC and DK CC calculations, the number of explicitly correlated electrons was equal to 16, 24, 26, and 26 for NaF, NaCl, RbF, and RbCl. This means that for NaF and NaCl only the 1s core electrons of Na and the halogen atom were left uncorrelated at the level of the CCSD(*T*) approximation. In the case of RbF the uncorrelated electrons are those of the *K*, *L*, 3s, and 3p shells of Rb and the 1s shell of F. In RbCl both the *K* and *L* shells of Cl are not correlated. To account for the electron correlation contribution due to energetically deeper shells, all-electron MBPT2 calculations have been carried out. The contribution of inner shells is then estimated as the difference between MBPT2 results for all electrons and those with the same number of correlated electrons as in the given CCSD(*T*) run. This approach has been used in several of our earlier calculations [20,30,32], and found to be satisfactorily accurate.

The perturbation strength values for the electric-field gradient perturbation in finite field perturbation calculations on NaF and NaCl were taken as equal to ± 0.0001 a.u. Slightly smaller values of ± 0.00005 a.u. are used for RbF and RbCl. In all calculations these values of the perturbation strength parameter give at least three stable decimals in the calculated electric-field gradients. In the case of the PCNQ model the nuclear quadrupoles have been placed as suggested in Ref. [9] with resulting nuclear quadrupole values of $\pm 0.05 \times 10^{-6}$ and $\pm 0.1 \times 10^{-6}$. The accuracy of the numerical differentiation scheme has been checked at the level of nonrelativistic calculations by comparing the results of the PCNQ model with those obtained in the finite-field perturbation scheme. The results are in complete agreement through at least three decimals.

The main part of our calculations has been carried out at the experimental values of the equilibrium bond distance, i.e., 3.639 514 a.u. for NaF, 4.461 258 a.u. for NaCl, 4.290 309 a.u. for RbF, and 5.340 928 a.u. for RbCl [40]. The derivatives of q^X have been obtained from the quartic fit to the q^X values computed at R_e , $R_e \pm 0.025$ a.u. and $R_e \pm 0.05$ a.u. All these results correspond to the level of the DK MBPT2 approximation with all electrons correlated. The values of the vibrational term q_1 of Eq. (4) are quite small and computing them at higher levels of theory does not seem to be necessary. Finally, let us mention that the software

used in present calculations is the MOLCAS system of quantum chemistry programs [42] and the set of CC programs TITAN [43].

III. RESULTS AND DISCUSSION

A. Electric-field gradients at Rb in RbF and RbCl

The main results of our calculations of the electric-field gradient at Rb in RbF and RbCl are presented in Table I. Both the nonrelativistic and relativistic DK results are included. The pattern of the electron correlation contribution to q^{Rb} is similar to that observed in calculations of q^K in KF and KCl [20]. The major part of the electron correlation effect is accounted for at the level of the second-order theory. It also follows from the comparison of the MBPT2, CCSD, and CCSD(*T*) data that the remarkably good performance of the MBPT2 approach is to some extent due to some mutual cancellations between different higher-order contributions. There seems to be no way to prove that the CCSD(*T*) result comes close to the limits of the electron correlation contribution to q^{Rb} . However, all experience with the results of this method indicates that its results are of exceptionally high quality [24,26]. One should also note that the error of about 10% in the calculated electron correlation contribution to q^{Rb} will lead to an order of magnitude smaller error in the final result. Hence improving upon the method of calculation of the electron correlation contribution to q^{Rb} is not expected to change the total computed values of this property significantly.

The relativistic effect on the electric field gradient at Rb is definitely not negligible. Most of it is accounted for at the level of the SCF HF approximation. The total relativistic effect on the electron correlation contribution to q^{Rb} , i.e., the effect of the interference between the bare nucleus relativistic terms and the Coulomb interaction between electrons, is very small for both molecules. One should remark that the calculations carried out in this study have been performed with the spin-free formulation of the DK theory [34]. Hence all our results neglect the effect of the spin-orbit coupling terms. However, it is rather unlikely that these terms may significantly contribute to q^{Rb} in almost completely ionic systems like RbF and RbCl. In support of this conclusion one should mention that in CsF the estimated spin-orbit contribution to the electric-field gradient at Cs amounts to only -0.0046 a.u. [21]. The leading part of this contribution is proportional to the square of the nuclear charge, and therefore should be an order of magnitude smaller in RbF (RbCl).

If the calculated results for q^{Rb} are to be used to obtain reliable values of $Q(\text{Rb})$, some assessment of their accuracy becomes of primary importance. Being convinced that there is no major fault on the side of methods used to compute the electron correlation and relativistic contributions, the main attention should be focused on some technical aspects of our calculations. One of the common mistakes in quantum-mechanical calculations for molecules is the use of insufficiently saturated basis sets. To rule out the possibility that the basis set devised for Rb and those used for F and Cl are insufficiently flexible for the purpose of the accurate calculation of q^{Rb} , we have carried out an extensive series of different tests. Most of the corresponding discussion will be presented for the RbCl molecule, for which the basis set

TABLE I. Calculations of the electric-field gradient at Rb in RbF and RbCl at the molecular equilibrium bond distance. All entries in a.u.

Method/Contribution	RbF			RbCl	
	NR	DK	NR	DK	DK
SCF HF/CC contributions ^a					
SCF	-1.342	-1.407	-1.015		-1.062
MBPT2	+0.106	+0.116	+0.056		+0.062
MBPT2(all) ^b	+0.095	+0.104	+0.048		+0.054
CCSD	+0.074	+0.074	+0.040		+0.044
CCSD(T)	+0.103	+0.103	+0.054		+0.058
CCSD(T)(est.) ^c	+0.092	+0.091	+0.046		+0.050
Nuclear		+0.228		+0.223	
Total electronic and nuclear ^d					
CCSD(T)	-1.011	-1.077	-0.743		-0.781
CCSD(T)(est.) ^c	-1.022	-1.089	-0.751		-0.788
Vibrational correction term ^e					
q_1		+0.013			+0.007

^aContributions calculated at the given level of approximation.

^bAll electrons correlated. The difference between the MBPT2(all) and MBPT2 results is used to estimate the electron correlation contribution due to the deep core electrons.

^cEstimated from the calculated CCSD(T) results and the MBPT2 contribution due to the deep core electrons.

^dThe total values are the sum of the SCF HF result, the electron correlation correction by the given method, and the nuclear contribution.

^eSee Eq. (4).

truncation effects are likely to be more important than for RbF.

The choice of basis sets made in the present study is based on the ionic model of the two rubidium halides. The halide ion is merely the source of the inhomogeneous electric field which introduces some asymmetry in the charge distribution around the Rb nucleus. Within such a model the description of the halide ion does not need to be highly accurate, and one can possibly use relatively small contracted basis sets. To check if the Cl basis set contraction provides enough flexibility and properly accounts for the electronic structure of the RbCl molecule, we have performed SCF HF calculations with completely uncontracted, i.e., (18s14p6d), GTO basis set of Cl. With such a basis set the nonrelativistic SCF HF result for q^{Rb} is -1.014 a.u., as compared to -1.015 a.u. calculated with the contracted set. In the case of RbF a similar calculation does not bring any changes within the number of reported decimals. Thus one concludes that the basis set contraction effect is unlikely to significantly affect the values of q^{Rb} presented in Table I.

Although RbF and RbCl are almost purely ionic species, the valence p -type orbitals of Rb can still make some contribution to the electric-field gradient at Rb. Since the basis set of Rb used in our studies has been generated under the assumption of a highly ionic character of the two molecules, it may not be flexible enough in the diffuse p part. This has been checked by performing nonrelativistic all electron MBPT2 calculations with the Rb basis set augmented with three diffuse p -type functions ($\zeta = 0.032\ 327\ 59$, $0.014\ 623\ 52$, and $0.006\ 615\ 01$). For RbCl such an extension makes q^{Rb} more negative by 0.004 a.u. at the SCF HF level. Simultaneously the MBPT2 all-electron correlation contribution becomes more positive by 0.003 a.u. than the result given in Table I. Thus, the net effect of the Rb basis set

extension is of the order of +0.001 a.u., and will not produce any major change of the calculated value of q^{Rb} in RbCl. The same must obviously hold for the RbF molecule whose ionic character is even more pronounced than that of RbCl.

Another possible source of inaccuracies in the calculation of q^{Rb} is the treatment of the electron correlation contribution due to deep core electrons. One may speculate that there will be some polarization of the $3s$ and $3p$ shells of Rb which may not have been properly accounted for at the level of the MBPT2 approximation. To check the validity of the present treatment of the electron correlation contributions due to these shells of Rb, we have carried out DK CCSD(T) calculations of q^{Rb} in RbCl for 42 explicitly correlated electrons. This means that the DK CCSD(T) treatment was extended to the L shell of Cl and the $3s$ and $3p$ shells of Rb. The contribution of the K and L shells of Rb and the K shell of Cl has been accounted for at the level of the DK MBPT2 approximation. The final estimate obtained from these calculations is $q^{\text{Rb}} = -0.785$ a.u., i.e., it differs from that given in Table I only by -0.003 a.u. In calculations of the nuclear quadrupole moment such a difference would result in the change of $Q(\text{Rb})$ by about 0.4%. Hence, extending the explicit high-level treatment of the electron correlation contribution to q^{Rb} to deeper electronic shells will not produce any considerable changes in the calculated value of $Q(\text{Rb})$.

All relativistic DK results of Table I have been obtained by using the PCNQ model [9], whose accuracy depends on the choice of charges which simulate the nuclear quadrupole. In order to verify the accuracy of the numerical differentiation of energies obtained with finite nuclear quadrupoles, we have used some higher values of the charges distributed around the Rb nucleus. The results have been found stable through the third decimal place.

TABLE II. Calculations of the electric-field gradient at Na in NaF and NaCl at the molecular equilibrium bond distance. All entries in a.u.

Method/Contribution	NaF			NaCl	
	NR	DK	NR	DK	DK
SCF HF/CC contributions ^a					
SCF	-0.755	-0.756	-0.634		-0.634
MBPT2	+0.037	+0.038	+0.020		+0.020
MBPT2(all) ^b	+0.037	+0.037	+0.020		+0.020
CCSD	+0.027	+0.027	+0.016		+0.014
CCSD(T)	+0.034	+0.034	+0.020		+0.018
CCSD(T)(est.) ^c	+0.034	+0.033	+0.020		+0.018
Nuclear		+0.373		+0.383	
Total electronic and nuclear ^d					
CCSD(T)	-0.348	-0.349	-0.232		-0.233
CCSD(T)(est.) ^c	-0.348	-0.349	-0.232		-0.233
Vibrational correction term ^e					
q_1		+0.007			+0.003

^aContributions calculated at the given level of approximation.

^bAll electrons correlated. The difference between the MBPT2(all) and MBPT2 results is used to estimate the electron correlation contribution due to $1s$ cores of the two atoms.

^cEstimated from the calculated CCSD(T) results and the MBPT2 contribution due to $1s$ cores of the two atoms.

^dThe total values are the sum of the SCF HF result, the electron correlation correction by the given method, and the nuclear contribution.

^eSee Eq. (4).

Additional support to the validity of the calculated data is also given by our experience with similar systems. Our recent calculations on KF and KCl [20] gave values of $Q(^{39}\text{K})$ resulting from the microwave spectra of the two molecules within 1 mb. The similar holds also in the case of the determination of $Q(^{73}\text{Ge})$ from the spectroscopic data for GeO and GeS [22]. All these data combined with the tests discussed in this section indicate that the DK CCSD(T) approach should be sufficiently reliable for calculations performed within the present study.

B. Electric-field gradients at Na in NaF and NaCl

In addition to calculating the molecular value of the nuclear quadrupole moment of Rb, the objective of the present study is also to complete the list of molecular values of the nuclear quadrupole moment for the alkali-metal nuclei. Most of these data are already available, although some of them have been obtained by using computational methodology which to some extent differs from the one used in this paper. The use of a uniform computational strategy becomes essential in the case of discrepancies between molecular values of Q and those derived from other sources. This is the case of the electric quadrupole moment of the ^{23}Na .

The molecular value of $Q(^{23}\text{Na})$ has been determined by Pyykkö and one of the present authors [19] from the q^{Na} data calculated for NaF and NaCl. Although these molecular results have been obtained at the level of the CCSD(T) approximation, the basis set design was considerably different from that used in the present case and in the case of our recent calculations for KF and KC [20]. Hence, in view of the existing discrepancy between different results for $Q(^{23}\text{Na})$ [19,44–47] and quite successful molecular cal-

culations for $Q(^{39}\text{K})$, it appeared worthwhile to repeat calculations of q^{Na} in NaF and NaCl in exactly the same framework as used for the other molecules. This will give molecular values of Q for Na, K, and Rb derived in essentially the same way, and will facilitate the discussion of our results for $Q(\text{Rb})$.

The main difference between the earlier calculations [19] of q^{Na} in sodium halides and analogous calculations for potassium and rubidium halides is the generation of GTO/CGTO basis sets. In the earlier study the Na basis set was partly contracted and the GTO/CGTO sets of F and Cl included the f -type functions [19]. The Na basis set devised for present calculations is fully uncontracted, i.e., it should have a similar flexibility as the sets used for K [20] and Rb. On the other hand, the GTO/CGTO sets for F and Cl used in this study are limited to s -, p -, and d -type functions, and may not be as flexible as the sets used in the earlier study of NaF and NaCl [19].

The results of present calculations with basis sets described in Sec. II are summarized in Table II. The pattern of the electron correlation contribution to q^{Na} follows that already discussed for q^{Rb} . The relativistic contributions are for both molecules almost completely negligible. For NaF the total DK CCSD(T) value of q^{Na} , including the MBPT2 estimate of the contribution due to $1s^2$ shells of the two atoms, is equal to -0.349 a.u., and compares very well with the earlier result (-0.347 a.u. [19]). The present DK CCSD(T) value of the total electric-field gradient at Na in NaCl is exactly the same as that given in Ref. [19]. Hence, in spite of certain methodological differences, our results for q^{Na} in NaF and NaCl are fully compatible with those of the earlier study. One should also mention that the earlier results for q^{Na}

TABLE III. ‘‘Molecular’’ values of the electric quadrupole moment of the ^{85}Rb and ^{87}Rb nuclei derive from the microwave data for RbF and RbCl and electric-field gradients calculated in this study.

$\nu_Q(\nu)^{a,b}$ (in MHz)	Source of $\nu_Q(\nu)^a$	$q^{\text{Rb}}(\nu)^c$ (in a.u.)	Isotope	$Q(\text{Rb})$ (in mb)
-70.341	$^{85}\text{Rb}^{19}\text{F}$, $\nu=0$	-1.082	^{85}Rb	276.4
-69.555	$^{85}\text{Rb}^{19}\text{F}$, $\nu=1$	-1.071	^{85}Rb	276.5
-68.779	$^{85}\text{Rb}^{19}\text{F}$, $\nu=2$	-1.058	^{85}Rb	276.5
-68.013	$^{85}\text{Rb}^{19}\text{F}$, $\nu=3$	-1.046	^{85}Rb	276.7
-67.259	$^{85}\text{Rb}^{19}\text{F}$, $\nu=4$	-1.034	^{85}Rb	276.8
70.739	$^{85}\text{Rb}^{19}\text{F}$, R_e^d	-1.089	^{85}Rb	276.4
	Recommended		^{85}Rb	276 ^e
-34.031	$^{87}\text{Rb}^{19}\text{F}$, $\nu=0$	-1.082	^{87}Rb	133.7
-33.684	$^{87}\text{Rb}^{19}\text{F}$, $\nu=1$	-1.071	^{87}Rb	133.9
-33.336	$^{87}\text{Rb}^{19}\text{F}$, $\nu=2$	-1.058	^{87}Rb	134.0
-33.336	$^{87}\text{Rb}^{19}\text{F}$, R_e^d	-1.089	^{87}Rb	133.7
	Recommended		^{87}Rb	134 ^e
-52.675	$^{85}\text{Rb}^{35}\text{Cl}$, $\nu=0$	-0.784	^{85}Rb	286
-52.306	$^{85}\text{Rb}^{35}\text{Cl}$, $\nu=1$	-0.777	^{85}Rb	286
-51.903	$^{85}\text{Rb}^{35}\text{Cl}$, $\nu=2$	-0.770	^{85}Rb	287
-52.884	$^{85}\text{Rb}^{35}\text{Cl}$, R_e^d	-0.788	^{85}Rb	286
	Recommended		^{85}Rb	? ^e
-25.485	$^{87}\text{Rb}^{35}\text{Cl}$, $\nu=0$	-0.784	^{87}Rb	138
	Recommended		^{87}Rb	? ^e

^aTaken from Ref. [5].

^bThe inaccuracies of the experimental data given in Ref. [5] do not influence the quadrupole moment values as reported in this table.

^cThese values correspond to the DK CCSD(T) approximation with the MBPT2 correction for the core contribution and the appropriate vibrational correction. See Table I.

^dExperimental estimate of ν_Q at the equilibrium bond distance R_e .

^eSee text.

in NaF and NaCl have been obtained only at the equilibrium bond distances and do not include vibrational corrections. The vibrational correction terms are, however, quite small (see Table II).

According to the present results for NaF and NaCl, one can conclude that the diminished flexibility of the F and Cl basis sets and the improved flexibility of the Na set are essentially of no importance for the calculated values of the electric-field gradient at Na. It follows from our earlier data for KF and KCl and from the present basis set analysis that the *spd* sets of F and Cl are flexible enough for accurate calculations of q at the alkali-metal atom in the studied series of the alkali-metal halides. Obviously their flexibility would be insufficient if we intended to calculate the field gradients at the halide nuclei. From the point of view of the alkali-metal atom in highly ionic halides, the halide ion is mainly a source of the inhomogeneous electric field which polarizes the density distribution in the vicinity of the alkali-metal ion. The covalent character of the metal-halide bond is less important, and can be well enough described in relatively small basis sets.

C. Electric quadrupole moments of the Rb and Na nuclei

The calculation of the electric quadrupole moment of the Rb nucleus is the main objective of this study, and the corresponding results are presented in Table III. The value of $Q(^{85}\text{Rb})$ derived from the data for RbF is in the range 276–

277 mb, and agrees with one of the two recommended values of the nuclear data tables (274 ± 2 mb) [10] which follows from atomic measurements of Feiertag and zu Pulitz [11]. This agreement shows that the other value of $Q(^{85}\text{Rb})$ given in these tables (263 ± 2 mb) [12,13] is most likely too low. One should point out that the $Q(^{85}\text{Rb})$ values derived by Feiertag and zu Pulitz [3,11] from the spectra of different low-lying $^2P_{3/2}$ excited states of the rubidium atom are consistently close to about 275 mb with estimated error bars of a few mb. For the ^{87}Rb isotope the present molecular value of Q derived from the RbF data (about 134 mb, Table III) also agrees with the experimental atomic results [3,13] which are in the range 131–133 mb with the estimated error of about 9 mb [13].

If our conclusions were based solely on the $Q(^{85}\text{Rb})$ value derived from the data for RbF the present calculations would lead to the recommended molecular value of the electric quadrupole moment of the ^{85}Rb nucleus equal to about 276 mb. According to the analysis presented in Sec. III A, the error bars, which result from different approximations involved in calculations of q^{Rb} , are unlikely to exceed about 1–2 mb. However, this is clearly contradicted by the result derived from the microwave data for RbCl; the value of $Q(^{85}\text{Rb})$ predicted from these data and the calculated electric-field gradient turns out to be by about 10 mb higher than the value derived from the RbF data. Although the difference between the nuclear quadrupole moments derived

TABLE IV. “Molecular” values of the electric quadrupole moment of the ^{23}Na nucleus derived from the microwave data for NaF and NaCl and electric-field gradients calculated in this study.

$\nu_Q(\nu)^{a,b}$ (in MHz)	Source of $\nu_Q(\nu)^a$	$q^{\text{Na}}(\nu)^c$ (in a.u.)	$Q(^{23}\text{Na})$ (in mb)
-8.4401	$^{23}\text{Na}^{19}\text{F}$, $\nu=0$	-0.346	103.9
-8.3279	$^{23}\text{Na}^{19}\text{F}$, $\nu=1$	-0.339	104.5
-8.2205	$^{23}\text{Na}^{19}\text{F}$, $\nu=2$	-0.332	105.3
-8.4980	$^{23}\text{Na}^{19}\text{F}$, R_e^d	-0.349	103.6
-5.6169	$^{23}\text{Na}^{35}\text{Cl}$, $\nu=1$	-0.228	104.6
-5.5614	$^{23}\text{Na}^{35}\text{Cl}$, $\nu=2$	-0.225	105.1
-5.4960	$^{23}\text{Na}^{35}\text{Cl}$, $\nu=3$	-0.222	105.4
	Recommended		104 ^e

^aTaken from Ref. [5].

^bThe inaccuracies of the experimental data given in Ref. [5] influence only marginally the quadrupole moment values reported in this table and are not taken into account.

^cThese values correspond to the DK CCSD(T) approximation with the MBPT2 correction for the core contribution and the appropriate vibrational correction. See Table II.

^dExperimental estimate of ν_Q at the equilibrium bond distance R_e .

^eSee text.

from the data for RbF and RbCl amounts to only about 4% one would not expect it to be that large. The experimental atomic result (132 ± 9 mb) [13] for the ^{87}Rb isotope is not very helpful because of rather large error bars; both molecular values of $Q(^{87}\text{Rb})$ determined in this study are well within the estimated error of the experimental data.

The strategy used in our earlier calculations and followed in the present study was to determine the molecular values of Q from the results for two different molecules [8,19,20,22]. They were found to agree within at least 1% or better. In the present case there is hardly any substantiated reason to expect that there is some major fault in our calculations of q^{Rb} in RbCl. These calculations are essentially similar to those which have been carried out recently for KCl. In the latter case the difference between the $Q(^{39}\text{K})$ values derived from the KF and KCl data was less than 1 mb; the value of $Q(^{39}\text{K})$ determined from the KCl data has been found marginally smaller than that derived from the KF quadrupole coupling constant [20]. There is no whatsoever indication that the electric-field gradients calculated for chlorides should be less accurate than those for fluorides. This is also confirmed by the present results for $Q(^{23}\text{Na})$ displayed in Table IV.

When discussing the possible sources of a rather large deviation between the $Q(^{85}\text{Rb})$ values determined from molecular data for RbF and RbCl, one may finally consider the possibility that the experimental values of the nuclear quadrupole coupling constants are not as accurate as claimed. In particular, the ^{85}Rb and ^{87}Rb coupling constants reported for RbCl are based on rather old measurements [17]. Their determination from the observed microwave spectra of RbCl involved several approximate assumptions in the fitting procedure. It would be worthwhile to repeat both the measurements and the determination of the Dunham-type series for the quadrupole coupling constant.

The present values of $Q(\text{Rb})$ derived from the experimental and theoretical data for RbF agree quite well with those obtained from atomic spectra [3]. Thus, we consider the $Q(\text{Rb})$ results which follow from the RbCl data as being significantly too high. The recommended molecular values of $Q(^{85}\text{Rb})$ and $Q(^{87}\text{Rb})$ presented in Table III are therefore based on the RbF data and equal to about 276 and 134 mb, respectively. The error bars of these values, though rather uncertain, are expected to be of the order of 1–2 mb. In view of relatively small differences between the theoretical molecular and atomic data for $Q(\text{K})$ [20,48] and consistent molecular results for $Q(\text{Na})$ [19] (see also Table IV) this estimate of inaccuracies is rather conservative.

There were two main reasons for the repeated calculation of the electric quadrupole moment for the ^{23}Na nucleus. One of them was to defend the earlier molecular result. Another one was to support the recent atomic calculations [46], which indicate that the so-called muonic value of $Q(^{23}\text{Na})$ is too low [44]. The earlier molecular value (104.2 mb) [19] has been found to be higher by about 4 mb than the result derived from the muonic experiment (100.6 mb) [44], which is believed to be accurate within ± 2.0 mb. The atomic value (107.1 ± 2.1 mb) of that time [45] was higher by about 3 mb than the value derived from molecular spectra. However, more recent improved atomic calculations of Jönsson *et al.* [46] have led to the reduction of the difference between atomic and molecular values of $Q(^{23}\text{Na})$ to about 1.4 mb, indicating that the muonic result may not be as accurate as expected [44,46]. One should also add that the molecular value of $Q(^{23}\text{Na})$ of Ref. [19] is in perfect agreement with much earlier atomic value of Salomonsson and Ynnerman (104.2 mb) [49]. To add to this variety of supposedly accurate data from Ref. [47], whose authors recently carried out relativistic many-body calculations of hyperfine constants for the sodium atom and derived another atomic value of $Q(^{23}\text{Na})$ equal to 101.4 ± 1.1 mb, almost matching that obtained in the muonic experiment.

The present molecular calculations, in spite of some methodological differences as compared to the earlier study [19], fully confirm the validity of the earlier result. According to the data of Table IV, the present most reliable value of $Q(^{23}\text{Na})$ is that derived from the quadrupole coupling constant of NaF at the experimental equilibrium bond length and the corresponding result for q^{Na} ; these data do not suffer from inaccuracies involved in approximate calculations of the vibrational correction term. The equilibrium value of the quadrupole coupling constant for NaCl is not available [5]. However, the pattern of changes observed for NaF indicates that the $Q(^{23}\text{Na})$ value, which would follow from the quadrupole coupling constant at R_e , would be a little below 104. This leads to the recommended molecular value of $Q(^{23}\text{Na})$ equal to about 104 mb, i.e., the same value as estimated in the earlier molecular study [19].

Combined with the improved atomic calculation by Jönsson *et al.* [46], this results supports the conclusion of these authors that the muonic result for $Q(^{23}\text{Na})$ is too low. The value of $Q(^{23}\text{Na})$ derived in Ref. [47] is rather close to the muonic result. However, the calculations of these authors neglected the contribution of triple excitations. There is no easy way to estimate the effect of these excitations on the atomic hyperfine constant. If we neglected the contribution

TABLE V. Electric quadrupole moments of alkali-metal nuclei. A comparison of different data. All values of Q in mb.

Nucleus ^a	Method of determination/Source			Recommended
	Molecular	Atomic	Other methods ^b	
⁷ Li	40.1 ^c	41 ± 6 ^d	40.3 ± 0.6 ^e	40.1 ^c
²³ Na	104 ^f	105.6 ^g	100.6 ± 2.0 ^h	104–105 ⁱ
³⁹ K	58.5 ^k	101.4 ± 1.1 ^j		59.5 ± 1 ^m
⁸⁵ Rb	276 ⁿ	60.1 ± 1.5 ^l		276 ^p
¹³³ Cs	−3.43 ^q	273 ± 2 ÷ 270 ± 17 ^o		−3.4–−3.7 ^s
²²³ Fr		−2.8, −3.3 ± 1.0, −3.7 ^r		
		1170 ± 10 ^t		

^aThe corresponding values for other isotopes can be derived from the known isotopic ratios of the nuclear quadrupole moment. See Refs. [3,5,7,8,20].

^bA very complete list of nuclear quadrupole moments can be found in Refs. [1,10]. However, most of these data are of very poor accuracy.

^cRecommended value based on the microwave data for LiH, LiF, and LiCl and computed electric-field gradients at Li [7,8,50]. See also Refs. [2,10].

^dIn spite of very accurate theoretical data [51] for the electric-field gradient at Li the atomic value is highly uncertain because of the inaccuracy of the experimental hyperfine splitting constant in the ²P state [3,52].

^eThe so-called “nuclear” value derived from nuclear scattering experiments [53].

^fThis paper. See also Ref. [19].

^gReference [46]. See text.

^hMuonic experiment (Ref. [44]). See text.

ⁱBased on present calculations and atomic results of Jönsson *et al.* [46]. Molecular results are consistently close to the lower value.

^jReference [47]. See text.

^kRecommended value based on the microwave data for KF and KCl and the calculated electric field gradients at K (Ref. [20]).

^lReference [48].

^mBased on molecular data of Ref. [20] and atomic data of Ref. [48]. A certain preference is attached to the lower value determined from molecular calculations.

ⁿThis paper. See text and Table III.

^oThe experimental atomic values derived from hyperfine splitting constants in different ²P_{3/2} states of Rb. See Ref. [3].

^pBased on calculations of this paper and analysis of different atomic data. See text.

^qCalculated from the microwave data for CsF and the computed electric field gradient at Cs (Ref. [21]).

^rSpectroscopic data from different sources whose accuracy is low and quite uncertain. See Ref. [3]. The newest value of Q (−3.7 mb) reported by Tanner and Wieman [54] is believed to be accurate within about 4%.

^sEstimated from molecular and atomic data with preference of the molecular value.

^tReference [55]. See text.

of triple excitations in our molecular calculations then [cf. the CCSD and CCSD(T) data of Table II], this would lead to the total (DK electronic and nuclear) q^{Na} values in NaF and NaCl equal to −0.356 and −0.233 a.u., respectively. Hence the value of $Q(^{23}\text{Na})$ would be lowered to about 102 mb, and would be in agreement with the result obtained in Ref. [47] in atomic relativistic SD calculations. This indirectly shows that indeed including the effect of triple excitations is needed for the improvement of the accuracy of the atomic value of $Q(^{23}\text{Na})$ derived by these authors. Most likely such atomic calculations would bring complete agreement between atomic and molecular values of $Q(^{23}\text{Na})$, and favor them over the experimental muonic value.

Finally, let us also point out that the molecular results for $Q(^{23}\text{Na})$ derived in this paper from two different sources are fully compatible with each other, and essentially the same as the earlier value [19]. In view of the discussion of differ-

ences between the two calculations the agreement between these results also supports the conclusion that the computed electric-field gradients in fluorides and chlorides should be of approximately the same accuracy. One would therefore expect that the Q values for Rb derived from RbF and RbCl should be close to each other. The observed differences (see Table III) are likely to be attributed to the inaccuracy of the old value of the quadrupole coupling constant derived from the microwave spectra of RbCl.

IV. ELECTRIC QUADRUPOLE MOMENTS OF THE ALKALI-METAL NUCLEI

The present determination of molecular values for $Q(\text{Rb})$ and the repeated determination of the nuclear quadrupole moment of sodium, combined with the earlier results for lithium [7,8] and potassium [20] and the very recent molecu-

lar data for cesium [21], complete the list of the corresponding molecular data for all stable alkali-metal nuclei. Thus a summary of these data and their comparison with those obtained from other sources appears to be both useful and timely. Such a comparison is presented in Table V.

The ${}^7\text{Li}$ nuclear quadrupole moment appears to be well established, and the agreement between the nuclear scattering [2,53] and molecular [7,8,50] values is quite satisfactory. It is worthwhile to recall that this agreement has been at least partly achieved due to molecular calculations [7,50] which indicated that the earlier experimental and theoretical nuclear values must be incorrect [7,50]. Also the atomic [46] and molecular [19] results for ${}^{23}\text{Na}$ and ${}^{39}\text{K}$ seem to have converged within about 1 mb. The results of the present paper fully confirm the earlier molecular result for ${}^{23}\text{Na}$.

The present molecular determination of the nuclear quadrupole moment of ${}^{85}\text{Rb}$ combined with the analysis of the atomic data strongly suggests that its value should be of about 276 mb. The error bars for this result should be of the order of 1 mb, as one would expect from the molecular data for other nuclei. The higher value of the quadrupole moment of ${}^{85}\text{Rb}$ derived from the microwave data for RbCl appears to indicate that the corresponding quadrupole coupling constant suffers from some inaccuracies. A new measurement of its value would most likely lead to the resolution of this problem.

The nuclear quadrupole moment of ${}^{133}\text{Cs}$ is quite small, and its determination from molecular data for CsF is believed to have error bars of the order of about 3% [21]. Similar error bars are also expected for the atomic value of Tanner and Wieman [54]. Both these data lead to the estimated value of the nuclear quadrupole moment of ${}^{133}\text{Cs}$ given in Table V.

With the present methods for high-level-correlated relativistic calculations of electric-field gradients in small molecules, the molecular determination of the nuclear quadrupole moment of Fr would be possible as well. However, the microwave data for molecules like FrF or FrCl do not seem to be available. The atomic values are known for a variety of isotopes [55]. They have been obtained by using experimental values of the B factor for the ${}^2P_{3/2}$ state and the calculated electric-field gradient [56]. For the most stable isotope,

${}^{223}\text{Fr}$, the nuclear quadrupole moment determined from these data is claimed to have a better than 1% accuracy. However, the uncertainty of the calculated electric-field gradient would not support such a high accuracy of the atomic result for $Q(\text{Fr})$.

V. SUMMARY AND CONCLUSIONS

In the study reported in this paper we have performed high-level-correlated relativistic calculations of the electric field gradient at Rb in RbF and RbCl. By combining these data with the spectroscopic values of the quadrupole coupling constant in these molecules, the molecular values of the nuclear quadrupole moment of ${}^{85}\text{Rb}$ and ${}^{87}\text{Rb}$ have been derived. A comparison of these data with those derived from atomic spectra leads to the molecular estimate of the nuclear quadrupole moment of ${}^{85}\text{Rb}$ as equal to about 276 mb. Simultaneously, the present analysis indicates that the experimental value of the nuclear coupling constant for RbCl is most likely too high by about 4% and the corresponding measurements need to be repeated.

The present study also confirms the reliability of the earlier molecular value of the nuclear quadrupole moment of ${}^{23}\text{Na}$. Together with the recent atomic calculations the present result for ${}^{23}\text{Na}$ shows that the inaccuracy of the muonic value of $Q({}^{23}\text{Na})$ is too low and less accurate than expected. The present results for Na and Rb combined with the earlier data for Li and very recent molecular calculations of $Q({}^{39}\text{K})$ and $Q({}^{133}\text{Cs})$ complete the list of molecular data for stable nuclei of the alkali metals, and lead to a compilation of the corresponding recommended values which concludes this paper.

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