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Quadrupole moments of the halogen nuclei

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The nuclear quadrupole moments for the isotopes of Cl, Br, and I were derived from theoretical calculations of the electric-field gradients in the simple diatomic molecules Cl_2, Br_2, and I_2. Two different density-functional methods, the full-potential linearized augmented plane waves and the projector augmented waves techniques were applied with various approximations for the exchange and correlation term. Using quadrupole coupling constants from the literature, the values for the nuclear quadrupole moments obtained are $|Q| = 8.19(11)$, 30.5(5), and 68.9(15) fm^2 for ^{35}Cl, ^{79}Br, and ^{127}I, respectively. Except for Cl the present results deviate considerably from formerly accepted values obtained from atomic spectroscopy. A reanalysis of the quadrupole coupling in the Cl, Br, and I atoms reveals the origin of this discrepancy.

I. MOTIVATION

Hyperfine interaction techniques, based on the observation of the coupling between nuclear moments and internal fields, have been widely used to study condensed matter on an atomic scale. The nuclear quadrupole interaction, in particular, can be a very precise measure of the electric charge distribution in molecules or solids. In such measurements the information is contained in the electric-field gradients (efg) V_{zz} acting at the nucleus. Directly accessible, however, is only the product of the nuclear quadrupole moment Q and the efg, the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$.

For investigations of the quadrupole interaction the halogen nuclei are particularly well suited. Chlorine, bromine, and iodine nuclei are the prime objects of nuclear quadrupole resonance studies. A very abundant data material is therefore available in the literature. Naively one would assume that the determination of the nuclear quadrupole moments of the nuclei involved had been made a long time ago. Actually the values for these critical constants cited in the most recent compilation[1] are in fact very old. Recently doubts on these ''standard'' values have been raised,[2,3] but also refuted.[4] It was the purpose of the present investigation to analyze the data for all three elements in a consistent manner in order to settle the discrepancies. The approach taken was to calculate the efg in the simple molecules Cl_2, Br_2, and I_2 and to compare them with critically evaluated experimental data of ν_Q in these molecules. The homonuclear diatomic molecules are the natural choice for the present purpose. The efg values are very large, of the order of the atomic ones, and the electronic structure has high symmetry, with identical charges at the two atoms. It is well known that for heteroatomic molecules the efg strongly depends on the charge transfer, a quantity that would therefore have to be calculated to high accuracy. The new values for Q derived in this work are found to deviate considerably from the ''standard'' values, except for Cl, where our result also agrees perfectly with recent calculations.

The present paper is organized as follows. In Sec. II we present our theoretical efg calculations; in Sec. III we critically evaluate the experimental data of the quadrupole coupling constants in the literature; in Sec. IV we present the quadrupole moments obtained combining the results from Secs. III and II; in Sec. V we attempt a reanalysis of the hyperfine interaction data for the halogen atoms; Sec. VI presents discussions and conclusions.

II. ELECTRIC-FIELD GRADIENT CALCULATIONS

The standard theoretical chemistry methods designed to study molecules are optimized in describing the chemical bonding. They usually suffer from a poor basis set near the nuclei and are thus not well suited to study hyperfine interaction parameters, in particular, for heavy nuclei. All-electron density-functional procedures have much fewer problems in treating heavy atoms. In the present paper, the theoretical calculations of the efg were performed using the full-potential linearized augmented plane waves (FLAPW) (Ref. 5) and the projector augmented waves (PAW) method,[6] both based on density-functional theory (DFT). The local density approximation (LDA) and different generalized-gradient approximations (GGA) were used with very similar results. The FLAPW method as embodied in the program package WIEN97 (Ref. 7) has been shown to yield reliable results for the band structure of various solids, in particular also for efg's (Refs. 8–11) in crystals. The PAW method is implemented in combination with the ''*ab initio*'' molecular-dynamics approach, and has proven to be a powerful technique for studying complex systems including molecules, surfaces, and solids. Recently, it has been demonstrated that the very efficient PAW method[12] is also able to give precise efg values.

The FLAPW method has been shown to be well suited in calculating the electron distribution in the solid state for periodic structures. To apply it to molecules one artificially constructs a large enough unit cell to effectively eliminate the interaction of the molecules. For precise calculations this

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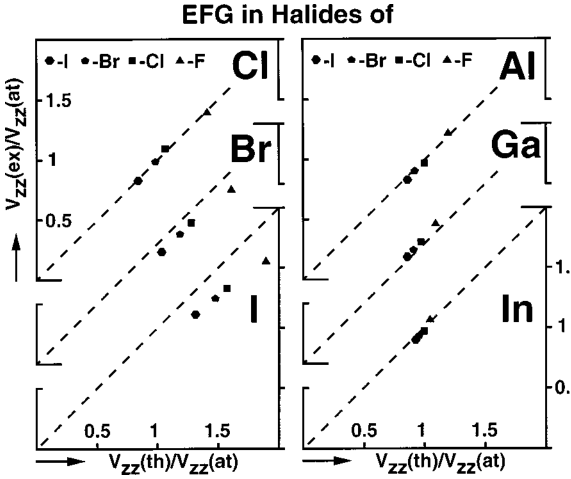

FIG. 1. Experimental efg for halides of Cl, Br, I, Al, Ga, and In calculated with ‘‘standard’’ Q versus the theoretical values, for presentation normalized with the atomic efg. The Hartree-Fock values used are 530, 939, 1164, 85.3, 226, and 349 V/Å^2.[14]

TABLE I. Total efg $V_{zz}{}^e$ in the halogen molecules, calculated with WIEN at the interatomic distances r_e. Also shown are the first and second derivatives of V_{zz} with respect to the interatomic distance (see text). For comparison we include the efg obtained in a nonrelativistic treatment V_{zz}(nrel) and the contribution of spin orbit interaction ΔV_{zz}(so), both normalized to $V_{zz}{}^e$.

	Cl_2	Br_2	I_2
r_e (Å)	1.9881(3)	2.2809(1)	2.666(1)
$V_{zz}{}^e$ (V/Å^2)	565(7)	1099(16)	1475(34)
$dV_{zz}/dr(V/\text{Å}^3)$	253	408	542
$d^2V_{zz}/dr^2(V/\text{Å}^4)$	−720	−993	−1170
V_{zz} (nrel)/$V_{zz}{}^e$	0.9761	0.9050	0.8000
ΔV_{zz}(so)/$V_{zz}{}^e$	−0.0000	−0.0067	−0.0273

requires separations that are several Å larger than the van der Waals distance. Since in the solution of the Kohn-Sham equations one then has to treat a large vacuum volume, this seems, in principle, to be not very efficient, requiring an extended plane-wave basis set and therefore large computer memory capacity and computing time. For the present application to small molecules, however, this is actually not a severe shortcoming, since the efficient numerical methods incorporated in the program packages still lead to easily manageable running times even for certainly large enough separations. It was checked that the limit of negligible molecular interaction was always reached for the results presented here. For the FLAPW calculations a primitive tetragonal cell was found as most appropriate, while the PAW results are for a cubic fcc cell. In the PAW calculation we also used a procedure that can correct for both the artificial electrostatic interaction of periodic images with themselves and the compensating charge background.[13]

In order to get an overview of the suitability of our approach, the efg at Cl, Br, and I, and also for comparison with Al, Ga, and In in all diatomic halides was calculated with LDA using an intermolecular separation of 2.4 Å larger than the respective interatomic distance. The experimental data, converted to efg with the ‘‘standard’’ values for Q, are plotted in Fig. 1 versus the calculated efg. The very good agreement for Cl, Al, Ga, and In is obvious. With the recently determined more accurate Q for Ga (Ref. 15) an even better agreement for the gallium molecules would be obtained. For the cases of Br and I, however, sizable systematic deviations are present, that could well be explained by using changed values for Q. The linearity of the curves in Fig. 1 indicates that the procedures adopted can definitely account for the relative efg at the same element in different molecules with high accuracy. In order to derive reliable values for Q, however, the absolute numbers are obviously needed.

For the reasons discussed above, the most reliable calculations can be made for the homonuclear dihalogens. Extensive calculations for the molecules Cl_2, Br_2, and I_2 were therefore performed with WIEN97. Three different approximations for the exchange and correlation term in the usual Kohn-Sham scheme of density-functional theory, LDA Ref. 16, GGA^{-1} Ref. 17 and GGA^{-2} Ref. 18, were used in order to get information about possible systematic errors from this source. The radius R_{MT} where the augmentation is performed was also varied for error analysis. All calculations were performed in the scalar relativistic approximation. For Br_2 and I_2 in addition the spin-orbit interaction within R_{MT} was included in a perturbative treatment. The interatomic distances r_e used, taken from experiment, are given in Table I, where the results obtained are summarized. For comparison with the results a nonrelativistic treatment, V_{zz}(nrel), as well as the difference between a calculation with and without spin orbit interaction ΔV_{zz}(so) are included. By calculating at slightly different internuclear distances r the first and second derivative of the efg relative to r was determined. Since these numbers were only needed for minor corrections to the final result and error analysis, as will be shown in the next section, no high precision was aimed for. The efg's for the same r_e were also calculated with the PAW method in the scalar relativistic approximation, being in all cases in very good agreement (less than 0.6%) with those obtained with WIEN97. With the same results from two completely independent DFT calculations, using different methods and programs, we can therefore proceed to investigate some discrepancies with former analysis of experimental data.

III. ANALYSIS OF EXPERIMENTAL DATA

The experimental number, in principle, directly available from experiment is the quadrupole interaction constant ν_Q in the free molecule in the vibrational and rotational ground state. Unfortunately this quantity has not been directly determined for the molecules investigated here. It has therefore been extracted from available experiments by various extrapolation procedures. The results, together with the estimated error given in parentheses, are summarized in Table II. Following Ref. 19 with the use of theoretical values of the efg at various interatomic distances (included in Table II) and standard molecular parameters [20] it is possible to make precise, albeit very small, corrections for vibrational and rotational excitation. These corrections applied to obtain the final experimental numbers are summarized in Table II, together with the theoretical effect of zero-point vibration.

Iodine. For the I_2 molecule we have the favorable situation that ν_Q in the vibrational ground state has been mea-

TABLE II. Quadrupole coupling constants $\nu_Q{}^o$ of the free diatomic molecules in the ground state extracted from available experiments. The references used to obtain these data are explained in the text. The corrections made to ν_Q and the theoretical zero-point corrections are also shown.

	$^{35}Cl_2$	$^{79}Br_2$	$^{127}I_2$
Experiment ν_Q (MHz)	102.45(15)	810.0(5)	2452.584(2)
Reference	ClBr (Ref. 25)	$\nu=1$ (Ref. 24)	$J=13$ (Ref. 23)
Correction	1.091(6)	0.9989(3)	0.999978(4)
$\nu_Q{}^o$ (MHz)	111.7(8)	809.1(7)	2452.530(11)
Zero-point correction	1.0017(4)	1.0011(3)	1.0010(3)

sured by various spectroscopic techniques.[21–23] The most precise data are for the $J=13$ rotational state. Thus only a slight correction to get the ground state value is needed.

Bromine. For the $\nu=1$ vibrational state ν_Q has been determined by microwave spectroscopy.[24] The correction for vibrational excitation is hardly larger than the experimental error.

Chlorine. Unfortunately for the free Cl_2 molecule no measurement of ν_Q is apparently available. There are precision data in the solid, but the intermolecular bonding is known to be quite appreciable in this case, leading even to an observable asymmetry parameter of the efg. Corrections for this solid state shift to the precision necessary for the present purpose appeared too uncertain. A different approach was therefore taken. For the molecule ClBr ν_Q at ^{35}Cl is known with high accuracy.[25] In theoretical calculations for the relative efg in similar molecules many sources of error are expected to cancel each other, leading to very precise predictions. The value used for ν_Q was therefore

$$\nu_Q(\mathrm{Cl}_2)=\nu_Q(\mathrm{CiBr})_{\mathrm{exp}}[\mathrm{efg}(\mathrm{Cl}_2)/\mathrm{efg}(\mathrm{CiBr})]_{\mathrm{th}},$$

where the ratio of the efg in Cl_2 and ClBr was taken from the FLAPW calculation. Various other calculations of this ratio with widely different procedures give essentially the same result, as shown in Table III. The assumption applied can be further checked by calculating ν_Q for Br_2 in the same way. The result is 811.3 MHz, in close agreement with the precise measurement (see Table II). It should be noted, however, that the present estimation of ν_Q for free Cl_2 as presented in Table II deviates considerably from previous extrapolations[27,28] making use of experimental systematics.

IV. RESULTING QUADRUPOLE MOMENTS

The calculation of the nuclear quadrupole moments by combining the calculated efg values with the experimental ν_Q values is straightforward. Since we have found a very minor, but systematic dependence of the efg values on the choice of density-functional parametrization, however, the final numbers are only quoted for the GGA^{-2} (Ref. 18) approximation. The actual numbers contain a small correction due to the fact that the measured ν_Q is not for the two nuclei at rest, but is reduced by zero-point vibration even for the $\nu=0$ state. This effect (see Table II) is, however, in all cases much smaller than errors in the theory. The major contribution to the estimated theoretical errors of V_{zz} given in Table I is definitely the uncertainty introduced by the necessary approximations in the density-functional treatment of the many-electron problem, difficult to estimate with confidence. As a representative quantity the difference between the use of various parametrizations for the exchange and correlation term was taken here. To the precision aimed for in the present analysis the inaccuracy of the scalar relativistic treatment and the effects of spin orbit interaction is also significant for the heavier elements. The uncertainty due to the actual choice of r_e, R_{MT}, and the separation between molecules is by comparison negligible.

TABLE III. Calculated efg ratio for BrCl to Br_2 and Cl_2 to ClBr obtained with four different methods. For comparison the available experimental result is also shown.

Method	Refs.	$BrCl/Br_2$	$Cl_2/ClBr$
SCF-LCAO	26	1.079	1.097
GAUSSIAN	4	1.073	1.081
PAW	(present)	1.089	1.087
FLAPW	(present)	1.080	1.091
Experiment	25	1.0816(8)	?

In Table IV the finally obtained quadrupole moments for ^{35}Cl, ^{79}Br, and ^{127}I are compared with earlier numbers in the literature.

For the different elements the following conclusions can be drawn.

Chlorine. The present result is close to the ''standard'' value and perfectly agrees with a recent analysis[32] of the atomic data using a many-electron calculation in $D_{\infty h}$ symmetry. Also calculations of molecular systems give very similar numbers.[4] It should be noted that by relying on a ν_Q value for Cl_2 determined via the theoretical ratio from the experimental result for ClBr we are effectively using this heteronuclear molecule as our reference. Fortunately the polarity of ClBr is quite small, however, so that the error from this source is still much smaller than the absolute error in the theoretical V_{zz}.

Bromine. Calculations for HBr (Refs. 2 and 3) have resulted in an appreciably smaller value for Q of ^{79}Br than formerly accepted. Though these molecular calculations face similar difficulties with a correct treatment of relativistic effects as the present work, there can be no doubt that the correct Q is lower than the previously accepted value.

Iodine. The ''standard'' value, cited as a private communication[31] by Stroke to Fuller in 1959, was determined from atomic data for the $P_{3/2}$ state and the then available relativistic correction factors. The later analysis of the same data by several authors[35,36] resulted generally in a

TABLE IV. Presently obtained nuclear quadrupole moments $|Q|$ (in fm^2) for ^{35}Cl, ^{79}Br, and ^{127}I as compared to earlier results, here classified as ''standard'', ''recent'', or ''other.''

	^{35}Cl	Refs.	^{79}Br	Refs.	^{127}I	Refs.
This work	8.19(11)		30.5(5)		68.9(15)	
''Standard''	8.249(2)	29	33.1(4)	30	78.9	31
''Recent''	8.165(10)	32	29.89	3	65.1	3
''Other''	7.6(5)	33	29.6(18)	34	64	35

smaller Q, but the numbers scatter widely. Calculations for the HI molecule[2,3] show a general tendency towards lower Q as well, but the results reported by the same authors differ considerably. As for Br, the major source for these differences is the uncertainty in the treatment of relativistic effects. Another recent relativistic calculation for I_2 (Ref. 37) gives an even larger V_{zz} than the present work, pointing again towards a considerable reduction of Q.

V. REANALYSIS OF ATOMIC DATA

Since the data for the hyperfine interaction constants $A_{3/2}$ and $B_{3/2}$ in the $P_{3/2}$ atomic ground state of the halogens Cl, Br, and I were already measured with high precision in the pioneering era in this field some 50 years ago,[38,34,39] it is clear that the first attempts of analysis suffered strongly from the inability to treat relativistic and many-electron effects at that time. Only some 25 years later was the relativistic electronic structure treatment being developed. Obviously it was also applied to the hyperfine interaction in the heavy halogens. Apparently the poor results for the magnetic hyperfine coupling obtained at that time, being strongly dependent on the calculational method used, discredited also the obtained values for Q. When data on the hyperfine coupling in higher atomic levels, in particular, the valence $P_{1/2}$ state, became available for Br and I in 1973/1975,[40] no serious attempt was apparently made to include them in the determination of Q. Actually the ground work for such an analysis has been laid by the relativistic Hartree-Fock (HF) calculations of Desclaux[41] and of Lindgren and Rosén.[42] Even the heuristic approach towards a more precise evaluation of Q was suggested.[42] We have analyzed the atomic data completely along these lines.

While without many-electron and relativistic effects the radial expectation value $\langle r^{-3}\rangle$ necessary for the calculation of the efg for a single electron or hole can simply be obtained from the magnetic hyperfine interaction, the complete description in the effective operator formalism requires five effective matrix elements, three for the magnetic interaction ($\langle r^{-3}\rangle_{01}, \langle r^{-3}\rangle_{12}, \langle r^{-3}\rangle_{10}$) and two for the electric interaction ($\langle r^{-3}\rangle_{02}, \langle r^{-3}\rangle_{11}$). The $\langle r^{-3}\rangle_{\kappa\lambda}$ are linear combinations of the radial integrals $\langle r^{-3}\rangle_{jj'}$ as defined in the theory of the relativistic hyperfine Hamiltonian by Sandars and Beck.[43] While in principle the magnetic parameters can all be determined from experiment for one p configuration (and have been for Cl), this is not so for the electric case. The technique suggested in Ref. 42 is to use the sum of the hyperfine parameters $A_{1/2}+A_{3/2}$, where effects of the direct spin contribution $\langle r^{-3}\rangle_{10}$ cancel, and calculate from experiment an effective $\langle r^{-3}\rangle_{01}$ through

TABLE V. Results of the analysis of atomic hyperfine structure data for ^{35}Cl, ^{79}Br, and ^{127}I. All entries are explained in the text.

	^{35}Cl	^{79}Br	^{127}I
I	3/2	3/2	5/2
$\mu_I(\mu_N)$	0.82086	2.0991	2.7937
$A_{3/2}$ (MHz)	205.05	884.81	827.265
$B_{3/2}$ (MHz)	54.873	−384.88	1146.356
$A_{1/2}$ (MHz)	1037.192	5336	6586
$\langle r^{-3}\rangle_{12}/\langle r^{-3}\rangle_{01}$	1.10	1.132	1.333
$\langle r^{-3}\rangle_{01\mathrm{HF}}\,(a_0^{-3})$	6.771	12.815	18.102
$\langle r^{-3}\rangle_{02\mathrm{HF}}\,(a_0^{-3})$	6.755	12.673	17.495
$\langle r^{-3}\rangle_{11\mathrm{HF}}\,(a_0^{-3})$	−0.140	−1.214	−4.080
$\langle r^{-3}\rangle_{B\ \mathrm{eff}}\,(a_0^{-3})$	7.097	13.267	17.147
Q_{At} (fm^2)	−8.227	30.87	−71.13

$$\langle r^{-3}\rangle_{01\mathrm{eff}}=(A_{3/2}+A_{1/2})2\pi(\mu_0\mu_B\mu_I{}^{*}\times[2+1.2\langle r^{-3}\rangle_{12}/\langle r^{-3}\rangle_{01}]),$$

where the ratio of the orbital to the spin-dipolar effect $\langle r^{-3}\rangle_{01}/\langle r^{-3}\rangle_{12}$ is taken either from experiment or from a relativistic HF calculation. By normalizing the calculated $\langle r^{-3}\rangle_{02}$, which makes the major contribution to the efg, by the ratio between effective and HF value for $\langle r^{-3}\rangle_{01}$, an effective $\langle r^{-3}\rangle_{02}$ is obtained. Together with a minor correction from the calculated $\langle r^{-3}\rangle_{11}$ one then has the needed value to calculate the efg and thus the relation between quadrupole moment and $B_{3/2}$:

$$\langle r^{-3}\rangle_{B\ \mathrm{eff}}=\langle r^{-3}\rangle_{02\mathrm{HF}}\langle r^{-3}\rangle_{01\ \mathrm{eff}}/\langle r^{-3}\rangle_{01\mathrm{HF}}+(5/36)^{1/2}\langle r^{-3}\rangle_{11\mathrm{HF}}.$$

Here we have added an index HF to denote a value obtained from the relativistic HF calculation.[42]

In Table V all the necessary data for the halogens are summarized. The results for Q obtained with

$$e^2Qh=5/2B_{3/2}/\langle r^{-3}\rangle_{B\ \mathrm{eff}}$$

for Cl, Br, and I are encouragingly close to the numbers obtained from the molecular analysis. Obviously it is very difficult to make a reliable error estimate, since the dominant source of uncertainty lies in the theoretical values used and the procedure adopted here.

VI. DISCUSSION AND CONCLUSIONS

From extensive theoretical calculations of the efg in diatomic molecules using two different approaches, combined with a careful analysis of the experimental measurements and from a reanalysis of atomic spectroscopy data we have obtained consistent values for the quadrupole moments of ^{35}Cl, ^{79}Br, and ^{127}I. The new values determined here may be used to calculate revised numbers for all other isotopes of the halogens by simply multiplying the experimentally determined ratios of the ν_Q values. In the case of iodine implications of the changed moments for the nuclear physics interpretation could be significant.

The present results call for additional experimental and theoretical investigations:

For chlorine a direct measurement of the ν_Q in the free molecule could eliminate the extrapolation needed in the present approach. It would also shed important light on the solid-state shift and the accompanying asymmetry parameter of the efg, an experimentally still controversial issue. It is well known that the standard density-functional procedures are inadequate for treating the van der Waals interaction. Existing FLAPW calculations for the solid halogens[44] thus do not properly account for all the available data.

Bromine obviously is a prime candidate for a more precise calculation of the efg in the free atom, as extension of the very successful work for lighter systems.[32]

The rather large quadrupole moment and its monoisotopic nature would make ^{127}I a good candidate for a direct measurement of the nuclear quadrupole moment by the muonic or pionic x-ray methods. The limited precision of the present value also leaves further room for improved analysis of the atomic data.

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