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REGULAR ARTICLE

The nuclear quadrupole moments of ^{191,193,195,197}Pb and ^{139}La

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Abstract The intermediate Hamiltonian coupled cluster method is applied to calculate the nuclear quadrupole moments (NQM) of Pb and La. Large, converged basis sets are used to get the electric field gradients at the relevant nuclei; these make possible the extraction of the NQM from the measured hyperfine coupling constant B. The only Pb NQM listed in Pyykkö's 2008 table (Mol Phys 106:1965, 2008) is for the neutron-rich unstable 209 isotope (halflife 3.25 h), given as −269(165) mb. This error bound of 60%, the largest in the table, comes from the poor precision of the measured B. More precise B values are now available for the neutron-poor isotopes with atomic weights 191, 193, 195, 197 and their NQMs are calculated herein. The best values obtained for these four isotopes are, respectively, 78(11), 179(9), 281(12), and 347(15) mb. The electric field gradient at the nucleus is the same for all Pb isotopes, so that NQMs of other isotopes may be evaluated when better B values become available for them. The same method is applied to ^{139}La, for which an accurate B value in the b^1D_2 state has recently become available. The calculated NQM is 206(4) mb, in excellent agreement with the recent molecular value of 200(6) mb.

Keywords Nuclear quadrupole moments · Coupled cluster method · Pb · La

1 Introduction

Nuclear quadrupole moments (NQM) are of considerable interest in spectroscopy, where they affect the hyperfine structure, and in nuclear physics, where they may be used to test nuclear structure models. Pyykkö [1, 2] has collected a critical list of all available data. The value quoted for ^{209}Pb, the only Pb isotope in the table, is −269(165) mb, with an error margin of over 60%, the largest in the list. This value appears in the CRC Handbook [3], quoted from the unpublished 1984 calculations of Doolen. A more comprehensive list of NQMs, including many stable and radioactive isotopes, has been given by Stone [4].

A well-known way to determine NQMs is by combining the experimental electric quadrupole coupling constant, B, with an accurate calculation of the electric field gradient (EFG) at the nucleus, q. The quadrupole moment Q may then be obtained from the relationship

$$B = -eQ/h, \qquad (1)$$

where e is the absolute value of the electron charge, and h is Planck's constant. B is usually known with great precision, and the accuracy of Q is determined by that of the calculated q. The case of ^{209}Pb is an exception, as the large uncertainty comes from the spectroscopic data, and does not even include the error margin in the calculated q, which is estimated at 25% [3].

Better precision was provided in the spectroscopy of the neutron-poor isotopes ^{195}Pb [5] and ^{191,193,197}Pb [6]. The B factor of the $^1D_2$ state has been obtained with 15% error limit for the 191 isotope and 5% for the other three.

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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A considerably larger uncertainty (25–60%) occurs for the $^3P_1$ state. Dutta et al. [6] calculated Q for these isotopes using Dirac-Fock (DF) EFG values [7]. The error in the resulting Q is put at 5%, as in the B values, but the uncertainty in the calculated EFG is 11% (see Eq. (8) in [6]), so the error margin in Q must be higher. An additional question occurs for isotope 191, for which the error in the calculated Q (6%) is lower than that of the measured B (15%). This may involve a typographical or other error.

The electric field gradient at the nucleus may be affected significantly by electron correlation, which is not included in the DF method. We have recently carried out high-accuracy calculations of NQMs for several atoms, including gold [8], the halogens Cl, Br and I [9], and the group-13 elements Ga and In [10], in which the relativistic coupled cluster method was applied in a large, converged basis to obtain reliable values of the EFGs and thus enhance the precision of the calculated NQMs. Here, we apply the method to the four Pb isotopes listed above. The EFGs calculated may serve for other isotopes, if hfs quadrupole coupling constants are measured with better precision.

The situation is different for lanthanum. Reasonably accurate hyperfine quadrupole coupling constants have been measured for the $^3P_1$, $^1G_4$, and b^1D_2 states of $^{139}\mathrm{La}^+$ [11, 12, 13], and a 1982 multiconfiguration Hartree–Fock calculation of the EFG gave an NQM of 200(10) mb [14]. The MCHF correlation corrections were calculated separately for each type of $(nl \rightarrow n'l')$ excitation and then added, and effects of relativity were estimated. It should be noted that the margin of error quoted in [14] reflects only the experimental uncertainties, ignoring the approximations in the EFG calculation, so that the actual error bounds may be significantly higher. More recently, a careful study of La monohalides [15], including correlation and relativity to high order, yielded $Q(^{139}\mathrm{La}) = 200(6)\mathrm{mb}$. The error quoted is the statistical standard deviation of the set of five molecules calculated, but the analysis in [15] points to a larger, unspecified systematic error. Here, we describe a high-level calculation of this NQM based on atomic spectroscopic data.

2 Methodology

The calculation of NQMs by the relativistic Fock-space coupled cluster method with single and double excitations, invoking the finite field approach, has been described before [8, 9, 10], and only a brief discussion will be given here. The 4-component Dirac-Coulomb Hamiltonian is used,

$$H_{DC} = \sum_i h_D(i) + \sum_{i>j} 1/r_{ij}, \tag{2}$$

where h_D is the one electron Dirac Hamiltonian. The interaction with an arbitrary NQM Q is added,

$$H(Q) = H_{DC} - eqQ/h, \tag{3}$$

so that the energy depends on Q,

$$E(Q) = \langle\psi(Q)|H(Q)|\psi(Q)\rangle = E_0 + Q(dE(Q)/dQ)_0 + \cdots. \tag{4}$$

Differentiating and invoking the Hellman–Feynman theorem, one obtains

$$(dE(Q)/dQ)_0 = -(e/h)\langle\psi_0|q_{zz}|\Psi_0\rangle, \tag{5}$$

assuming higher-order derivatives may be neglected. The required expectation value of the EFG is thus obtained from the first derivative of the energy with respect to the NQM.

It should be noted that the value of Q used in Eq. (3) is *not* the physical NQM. It is selected so that the linearity of $E(Q)$ is maintained, while the energy change is sufficiently large to provide good numerical precision. Linearity is checked by repeating the calculations with several Q values. The external field is included from the start and affects the Dirac-Fock orbitals. Attempts to include it only at the coupled cluster level were less satisfactory.

3 Calculations and results

3.1 Pb

For Pb, we started from the closed shell Pb^{2+} as the reference state of the Fock-space coupled cluster calculations. The intermediate Hamiltonian coupled cluster method [16, 17] was used to make possible large model spaces. The main model subspace P_m included all states obtained by adding two electron in the 7*s*, 8*s*, 6*p*, 7*p*, and 6*d* orbitals; the full model space P included, in addition, all states with occupied 9*s*–12*s*, 8*p*–11*p*, 7*d*–9*d*, 5*f*–7*f*, and 5*g* orbitals. The uncontracted well-tempered Gaussian basis set [18] was used. It was increased, adding functions with both larger and smaller exponents, until the calculated EFG converged to better than 0.5%. The final basis included 28*s*24*p*21*d*14*f*7*g* functions. The contribution of *h* basis functions was negligible (<0.3%). The 64 external electrons were correlated, and only the 18 inner shell electrons were frozen in the DF orbitals. Virtual orbitals with energy above 100 a.u. were discarded at the CC stage. The values used for Q in Eq. (3) were 0, 5×10^{-6}, and 1×10^{-5} a.u., and the deviation from linearity was below 0.1%. The EFG was obtained for the $^1D_2$ and $^3P_1$ states, for which B values are available [5, 6]. The final calculated EFG values are 6.697 a.u. in the $^1D_2$ state and 0.5897 a.u. in $^3P_1$. In line with our previous NQM calculations [8, 9, 10], we estimate

Table 1 B (in MHz) and Q (in mb) of Pb isotopes

Mass	$^1D_2$ state			$^3P_1$ state		
	B [5, 6]	Q [6]	Q present	B [5, 6]	Q [6]	Q present
191	123(18)	85(5)	78(11)	−15(8)	130(80)	108(58)
193	282(14)	195(10)	179(9)	−19(7)	160(70)	137(51)
195	442(19)	306(15)	281(12)	−33(9)	290(100)	268(34)
197	546(23)	378(19)	347(15)	−59(12)	510(130)	426(87)

the remaining error at ~2%, which is smaller in this system than the error limits of the experimental coupling constants (5% for the $^1D_3$ state, much higher for $^3P_1$).

Table 1 shows the available hyperfine coupling constants and calculated NQMs for isotopes of Pb. To compare with Ref. [6], the error margins are those of the measured B; the error in the EFG is much smaller. The NQMs calculated here are about 10% lower than those reported in [6] using the DF EFGs, reflecting the increase in the EFG upon including correlation. The value 85(5) mb, listed in [6] for isotope 191, seems to have a too low error margin, which cannot be lower than the error in B (see Sect. 1). The measurements in the $^3P_1$ state are less precise than for the $^1D_2$ state and yield less precise NQMs, but the values obtained from the two states agree within their error margins. The Q values obtained from the $^1D_2$ data are the best available for any Pb isotope.

3.2 La

Höhle et al. [11] reported the electric quadrupole coupling constants of the $^3P_1$, $^1G_4$, and b^1D_2 states of ^{139}La$^+$ with ~4% precision, giving B values of 25.8 ± 0.9, 151.7 ± 5.4, and 39.9 ± 1.8 MHz, respectively. Much better precision (0.04%) was achieved for the last state by Schef et al. [13], who obtained 39.043 ± 0.013 MHz. These three states are the target of our calculations.

Starting from the La^{3+} closed shell ion, the states of the monocation are reached by adding two electrons in the 5d and 6s shells. The P space comprises all determinants obtained in this manner. The convergence of the EFG with the basis is demonstrated in Table 2. The g functions have significant contributions, whereas the effect of the h functions is negligible. The final basis includes 30 s, 23 p, 23 d, 14 f, and 9 g uncontracted Gaussians, taken from the well-tempered series [18]. The outer 39 electrons were correlated, while the 18 inner shell electrons (1s2s2p3s3p orbitals) were frozen at the coupled cluster stage, and virtual orbitals above 100 hartree were discarded. Using the calculated EFGs, the Q values obtained from the reported coupling constants for the $^3P_1$, $^1G_4$, and b^1D_2 states were 206, 221, and 206 mb, respectively, which coincide within the experimental error limits of the B measurements [11, 13]. Since the uncertainty in B of b^1D_2 is just 0.04%, compared with ~4% for the other two states, the Q obtained for this state is adopted. With the error in calculating the EFG estimated at ~2%, the final value of the ^{139}La is 206(4) mb, in very good agreement with the molecular value [15] of 200(6) mb.

4 Summary and conclusion

The relativistic coupled cluster and its intermediate Hamiltonian extension have been applied to calculate the electric field gradients at the ^{191,193,195,197}Pb and ^{139}La nuclei, needed to obtain the nuclear quadrupole moments of these atoms from measured hyperfine electric coupling constants B. The situation in Pb is unusual, with the error margin in B much larger than for the calculated EFG.

Table 2 Convergence of the EFG and Q in the ^{139}La b^1D_2 level

Basis	s	p	d	f	g	h	EFG (au)	Q (mb)
30s23p22d14f	1–30	5–27	8–29	13–26	–	–	0.7787	213
30s24p22d14f	1–30	4–27	8–29	13–26	–	–	0.7787	213
30s24p22d14f	1–30	5–28	8–29	13–26	–	–	0.7787	213
30s23p23d14f	1–30	5–27	7–29	13–26	–	–	0.7723	214
30s23p23d14f	1–30	5–27	8–30	13–26	–	–	0.7789	213
30s23p22d15f	1–30	5–27	8–29	12–26	–	–	0.7785	213
30s23p22d15f	1–30	5–27	8–29	13–27	–	–	0.7783	213
30s23p22d14f7g	1–30	5–27	8–29	13–26	18–24	–	0.8250	201
30s23p22d14f7g2h	1–30	5–27	8–29	13–26	18–24	20–21	0.8250	201
30s23p22d14f8g	1–30	5–27	8–29	13–26	17–24	–	0.8250	201
30s23p22d14f8g	1–30	5–27	8–29	13–26	18–25	–	0.8100	205
30s23p22d14f9g	1–30	5–27	8–29	13–26	18–26	–	0.8079	206

The n values in the well-tempered basis [18] are given

Nevertheless, NQMs for the neutron-poor isotopes can be calculated, giving the best estimates to date for any Pb isotope. Better NQMs may be derived when more precise hyperfine constants become available for these and other isotopes. For ^{139}La, we obtain a NQM of 206(4) mb, in very good agreement with the recent molecular value of 200(6) mb.

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