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Research paper

Accurate determination of the nuclear quadrupole moment of xenon from the molecular method

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ABSTRACT

This study provides a new determination of the nuclear electric quadrupole moment (NQM) for ^{131}Xe, which is achieved by the molecular method. Dirac-Coulomb Coupled Cluster calculations with a Gaunt correction (DC+G-CC) of electric field gradients (EFGs) and experimental nuclear quadrupole coupling constants of six molecular systems (XeH^+, XeCuF, XeCuCl, XeAgF, XeAgCl and XeAuF) were considered. The best NQM obtained by our DC+G-CCSD-T EFGs was −114.6(1.1) mbarn, which is recommended as the new reference value for this nuclide given the high level electron structure calculations done here.

1. Introduction

An easy way to gain access to information about the nuclear charge distribution of specific atoms is through their nuclear electric quadrupole moment (NQM) values. Hence, this property has been determined for several nuclides and the 'atomic' or 'molecular' methods are usually employed to this end [1,2]. These methods depend on the association of state-of-art electronic structure calculation results and trustworthy experimental data of atomic or molecular systems [3].

The study regarding xenon started in 1961 with Faust and McDermott [4], who found a NQM of −120(12) mbarn for the ^{131}Xe nucleus. Almost forty years later, in 2000, Paduch and Bieroń [5] reviewed this quantity and deduced a new value, −117(6) mbarn. However, it is important to point out that these previous determinations were based on the atomic method. On the other hand, a NQM of −114(1) mbarn was calculated in the last investigation, which was now performed with the molecular method by Kellö et al. [6] in 2001 . These authors used data of two molecules (XeH^+ and XeD^+) and two-component coupled cluster (CC) calculations. Actually, this is the recommended value for ^{131}Xe [2].

Nevertheless, two distinct approaches can be used to evaluate the NQM within the molecular method. The direct variant consists in the prompt combination (one molecule at a time) of high level calculations of electric field gradients (EFGs) at the position of a specific nucleus X and accurate data of experimental nuclear quadrupole coupling constants (NQCCs) by the equation

$$Q(X) = \frac{\nu_Q(X)}{234.9647 q(X)}, \quad (1)$$

where $Q(X)$, $\nu_Q(X)$ and $q(X)$ are, respectively, the NQM (in barns), the NQCC (in MHz) and the EFG (in a.u.) of X in a linear molecule. The direct approach can be used even if the NQCC was measured for a single molecule, although more reliable results require averaging the NQMs from more systems. However, some care must be taken with this alternative once inappropriate electronic structure treatments can lead to significant systematic errors in EFGs [7]. The other way to determine NQMs with the molecular method is the indirect version. In this case, the NQM is essentially achieved by means of linear regressions between NQCCs and EFGs obtained for a group of molecules containing the nucleus under study [8]. Thus, this approach is considered as more robust than the direct one [9] taking into account the fact that calculations of EFG variations among compounds are generally more reliable than those of absolute EFG values of individual molecules. However, the molecular systems used in the indirect version should present enough diversity to result in satisfactory regression parameters. In this context, the NQM determination of ^{131}Xe mentioned previously [6] was attained with the direct version of the molecular method.

In this investigation we decided to select six linear molecules containing xenon (XeH^+, XeCuF, XeCuCl, XeAgF, XeAgCl and XeAuF) to provide a revision of the NQM for ^{131}Xe by means of the molecular method. Moreover, the EFG values used here are obtained through more advanced relativistic electronic structure calculations, which are derived from the four-component Dirac-Coulomb (DC) formalism with a Gaunt correction (DC+G), along with the coupled cluster theory with iterative single and double

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substitutions and perturbative treatment of triple excitations (CCSD(T) and CCSD-T).

2. Computational details

All calculations were done with the DIRAC14 package [10] by means of a standard speed-of-light value of 137.035 999 8 a.u. and the uncontracted form of all basis sets. A new relativistic prolapse-free basis set of quadruple-ζ quality (RPF-4Z) was initially selected for xenon (25*s*21*p*14*d*2*f*1*g* large functions) [11], while the remaining elements are described by the choices listed in Table 1 [12–17].

The Dirac-Coulomb (DC) Hamiltonian was used in almost all calculations performed here, while the Dirac-Coulomb-Gaunt (DG) Hamiltonian was only considered at the Hartree-Fock (HF) level. Thus, the effect of the Gaunt term, which is evaluated by differences between DG-HF and DC-HF EFGs, is added to our results including electron correlation (treatment labelled as DC+G). The two-electron integrals of small functions, (SS|SS), were replaced by an interatomic correction [18]. Second-order Møller-Plesset Perturbation Theory (MP2) and the Coupled Cluster approach with iterative single and double substitutions along with a perturbative correction for triple ones (CCSD-T and CCSD(T)) were used to achieve an advanced description of electron correlation effects. Moreover, the smallest active space considered in the calculations encloses the spinors with energy between −3.5 and 20.0 a.u., corresponding to the valence and some of the sub-valence electrons of xenon (5*s*, 5*p* and 4*d*) and the other atoms. This active space includes from 18 to 42 electrons depending on the molecule.

Analytical expressions were employed to obtain EFGs at HF and Density Functional Theory (DFT) levels, using the B3LYP, PBE0 and PBE0q functionals [19–23]. Moreover, since DIRAC14 does not provide analytic EFG results for CC calculations, we estimated the electron correlation contributions to EFGs (Δq_{corr}) with the finite-difference technique in a two-point form,

$$\Delta q_{corr} = \left(\frac{\partial E(\lambda)}{\partial \lambda}\right)_0 \approx \frac{E(+\lambda) - E(-\lambda)}{2\lambda}, \quad (2)$$

where E is the correlation energy and the perturbation, λ, was taken as 1.0×10^{-7} a.u. after a few tests. Finally, the geometries and NQCCs adopted in our calculations are described in Table 2 [24–27].

3. Results and discussion

3.1. Xenon basis set increment

Customarily, a previous basis set convergence study is required to achieve accurate EFG determinations. This step is performed with DC-HF and DC-B3LYP calculations for XeH^+ and investigates the need for any complementation of the xenon basis set in order to provide a satisfactory description of this challenging property that requires, among other aspects, a proper treatment of the innermost atomic region.

Table 1
Basis sets selected for EFG calculations.

(Xe– M – X)[a]	M	X
XeH^+	cc-pVQZ	
XeCuF	cc-pVTZ	cc-pVTZ
XeCuCl	cc-pVTZ	cc-pVTZ
XeAgF	dyall.v3z	cc-pVTZ
XeAgCl	dyall.v3z	cc-pVTZ
XeAuF	dyall.v3z	cc-pVTZ

[a] M refers to hydrogen or a metal (Cu, Ag or Au) while X is an halogen (F or Cl).

Table 2
Bond lengths adopted in EFG calculations (Å), r, NQCC values at the ^{131}Xe nucleus (MHz) and the number of electrons in the smallest active space considered.[a]

Molecules	r(Xe – M)[b]	r(M – X)[b]	NQCC	Electrons[c]
XeH^+[d]	1.6028		−370.55	18
XeCuF[e]	2.4327	1.754	−87.78	42
XeCuCl[e]	2.471	2.058	−81.4	42
XeAgF[f]	2.6633	1.9799	−82.85	42
XeAgCl[f]	2.7106	2.2714	−78.17	42
XeAuF[g]	2.5483	1.918	−134.54	42

[a] M refers to hydrogen or a metal (Cu, Ag or Au) while X is an halogen (F or Cl).
[b] The bond length for XeH^+ refers to the equilibrium structure while the data for the remaining systems are associated to the ground vibrational level.
[c] Number of electrons included in the smallest active space.
[d] Ref. [24].
[e] Ref. [25].
[f] Ref. [26].
[g] Ref. [27].

Tighter and more diffuse Gaussian functions of each angular momentum (*s*, *p*, *d*, *f* and *g*) were analyzed in this case, each kind at a time. The exponents of these functions are easily obtained by means of extrapolations from the polynomial parameters that define each of these function symmetries in the RPF-4Z set [11]. Hence, nine tight *f* functions (exponents: 1.098347412, 2.264263413, 4.465417330, 8.540532713, 16.05963189, 30.09912342, 57.00063067, 110.5739801 and 222.7478948) and two tight *g* functions (exponents: 0.8283867782 and 1.762025943) were added to the original RPF-4Z of xenon, which results in an extended set with 25*s*21*p*14*d*11*f*3*g* large functions to be used in analytical EFG determinations. It is important to notice that any function capable of causing EFG variations equal or larger than 0.005 a.u. in DC-HF or DC-B3LYP calculations was included (around 0.04% of DC-HF or DC-B3LYP EFGs). The EFG values associated to the chosen functions are presented in Table 3.

However, although this basis set is quite accurate for EFG determinations at the xenon nucleus, the tightest *p* and *d* functions can sometimes induce some disturbances in the electron correlation contributions derived from Eq. (2) [28,29]. Thus, a comparative analysis of xenon EFG values obtained from the finite-difference technique and analytical expressions, which was done by means of DC-HF calculations in XeH^+, showed that just the tightest *p* function must be removed to attain stable numerical results. Therefore, the numerical calculations presented in this work, which are based on Eq. (2), used a slightly smaller basis set for xenon (25*s*20*p*14*d*11*f*3*g*).

3.2. Electric field gradients

The EFGs calculated at the position of the xenon nucleus in each molecule are shown in Table 4. First, one should notice that the EFGs obtained with the Gaunt term (DG-HF) are always smaller than those values found without this correction (DC-HF) by 0.5–1.0%. Hence, this relativistic contribution seems already important if one intends to reach accuracies around 1% for xenon. The relevance of the Gaunt term for EFG determinations was previously evidenced by Pernpointner [30]. Furthermore, since electron correlation is normally as important as relativity for EFG calculations, high level treatments such as CCSD(T) and CCSD-T were used to determine the contribution of this effect to the resulting values. In addition, EFGs were also obtained at the DC-MP2 level with a nearly complete active space (all electrons and virtual spinors up to 100 a.u.). Thus, this active space increment provokes an increase of EFGs from 1.1 to 2.5% at the DC-MP2 level. The relevance of this factor certainly demands the provision of a full active space correction to CC EFG values, which was given by