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# Nuclear electric quadrupole moment of $^{45}\text{Sc}$ : reconfirmation and extension to diatomic ScN

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**The nuclear electric quadrupole moment (NEQM)  $eQ$  of  $^{45}\text{Sc}$  is redetermined as  $-223(3)$  mb at CCSD-T level using a data set of the diatomic molecules ScF, ScCl, ScBr and ScN.**

The nuclear properties of scandium are of current interest.<sup>1</sup> The present standard value of  $eQ(^{45}\text{Sc})$ ,  $-220(2)$  mb was determined in 2000 by Kellö *et al.*<sup>2</sup> using experimental data on the diatomic ScF, ScCl and ScBr, combined with electric field gradient (EFG) calculations performed at the CCSD(T) level employing the Douglas–Kroll one-component approximation. Here, we confirm these earlier calculations using a four-component Dirac–Coulomb Hamiltonian and add one more data point on diatomic ScN from a later measurement.

A detailed description of the methodology can be found in our previous publication on  $eQ(^{209}\text{Bi})$  and  $eQ(^{121}\text{Sb})$ .<sup>3</sup> Here, we provide a brief summary of the key steps used to calculate the nuclear electric quadrupole moment of  $^{45}\text{Sc}$ .

In a diatomic molecule, the total electric field gradient eq (EFG) at nucleus  $X$  is expressed as the sum of nuclear and electronic contributions:

$$q(X) = q_{\text{nuc}}(X) + q_{\text{el}}(X) \quad (1)$$

In this work, the electronic contribution along the molecular axis at the location of the nucleus  $X$   $q_{\text{el}}(X)$ , was computed using the DIRAC program package,<sup>4</sup> employing both a relativistic coupled-cluster method (CCSD-T) and density functional theory (DFT) with the PBE0 functional.<sup>5,6</sup> All calculations were performed using the default thresholds, convergence criteria and DFT grids of the DIRAC program.

The CCSD-T method, originally developed by Deegan and Knowles,<sup>7</sup> improves upon the conventional CCSD(T) by including more disconnected triple excitations up to fifth order. This approach has been shown to yield more accurate EFG values.<sup>8</sup>

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CCSD-T calculations were carried out using uncontracted Dyall CV3Z basis sets.<sup>9,10</sup> In the CCSD-T calculations, core electrons were frozen, valence electrons were correlated (orbitals in the  $-3.5$  to  $3.5$  Hartree energy range were included in the active space). Our DFT calculations employed uncontracted Dyall 3ZP basis sets.<sup>9,11</sup> A Gaussian nuclear charge distribution model was applied. All calculations were performed using the closed-shell ground state  $X^1\Sigma^+$  at experimental equilibrium bond lengths  $R_e$ , as listed in Table 1.

In DFT, the EFG was obtained analytically, as implemented in DIRAC. For the CCSD-T method, the EFG was calculated by combining the analytic Hartree–Fock (HF) contribution with a correlation correction  $q_{\text{el}}(X) = q_{\text{el, HF}}(X) + q_{\text{el, corr}}(X)$ . The latter was evaluated by fitting correlation energies computed at a range of external electric field strengths ( $\pm 1.0 \times 10^{-6} E_h/ea_0^2$  and  $\pm 1.0 \times 10^{-10} E_h/ea_0^2$ ) to an 5th-order polynomial and extracting the first-order response, following the approach of Arcisauskaitė *et al.*<sup>17</sup>

Finally, the nuclear electric quadrupole moment was derived using the indirect method,<sup>18,19</sup> which involves fitting a linear regression to experimental nuclear quadrupole coupling constant (NEQCC) across a series of compounds:<sup>3</sup>

$$\text{NEQCC}[\text{in MHz}] = 0.2349647 \times eQ[\text{in mb}] \times eq[\text{in } E_h/a_0^2] \quad (2)$$

This combined strategy incorporating both a polynomial fit for the correlation correction and an indirect determination of

**Table 1** Available experimental nuclear quadrupole coupling constants (NEQCC) at the equilibrium bond length  $R_e$  in  $^{45}\text{Sc}$  diatomic molecules

| Molecule                       | NEQCC (MHz) | $R_e$ (Å)          | Ref.      |
|--------------------------------|-------------|--------------------|-----------|
| $^{45}\text{Sc}^{19}\text{F}$  | 74.0861(51) | 1.787 <sup>a</sup> | 12 and 13 |
| $^{45}\text{Sc}^{35}\text{Cl}$ | 68.2067(29) | 2.23029467(95)     | 13        |
| $^{45}\text{Sc}^{79}\text{Br}$ | 65.2558(32) | 2.3808465(10)      | 14        |
| $^{45}\text{Sc}^{14}\text{N}$  | 33.818(19)  | 1.68723(3)         | 15 and 16 |

<sup>a</sup> No standard deviations were given.



**Table 2** The contributions (in  $E_h/ea_0^2$ ) to the electric field gradient at Sc in ScF, ScCl, ScBr and ScN at experimental values of the equilibrium bond length

| Contribution           | ScF     | ScCl    | ScBr    | ScN     |
|------------------------|---------|---------|---------|---------|
| Nuclear                | 0.4674  | 0.4542  | 0.7686  | 0.4319  |
| Electronic DC-HF       | -2.1815 | -2.0062 | -2.2571 | -0.3645 |
| Correlation correction | 0.2760  | 0.2570  | 0.255   | -0.7230 |
| Total                  | -1.4381 | -1.2951 | -1.2335 | -0.6556 |

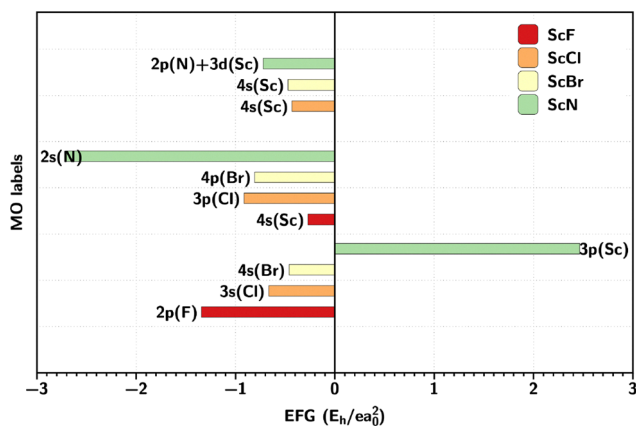
the NEQM serves to mitigate potential sources of error at each stage of the evaluation.<sup>3</sup>

The nuclear, electronic HF and CCSD-T correlation contributions, to the electric field gradient at Sc in ScF, ScCl, ScBr and ScN are summarised in Table 2.

The analysis of this table highlights the unique behavior of ScN compared to other compounds in the ScX series. First, the electronic component  $q_{el,HF}$  is only slightly negative, in contrast to the other compounds. Furthermore, ScN turns out to be a strongly correlated system. These results can be attributed to the presence of a triple bond in ScN, involving four  $\pi$ -electrons.<sup>20</sup> This can be observed through the analysis of the orbital contribution to the EFG value shown in Fig. 1. These analyses are only possible from analytical calculation of the EFG. Bast and Schwerdtfeger computed the EFG at scandium in ScX (X = F, Cl, Br, I, H, Li) using density functional theory and analyzed the orbital contributions in ScF.<sup>21</sup> Here they were done with DFT/PBE0 calculations.

A general observation is that the dominant contribution to the EFG arises from valence electrons. This has been previously reported—for example, by Neese *et al.*<sup>22</sup> in their study of HI and HAT where the majority of the observable field gradient was found to originate from the core region of the valence orbitals. A similar conclusion was obtained in our previous investigation of <sup>209</sup>Bi and <sup>121</sup>Sb.<sup>3</sup>

For the ScX halide series, the EFG value originates from the 2p (F), 3s (Cl), 3p (Cl), 4s (Br), and 4p (Br) orbitals. ScN behaves very differently. As previously discussed, it is a strongly bound system, and the EFG value is determined by the orbital mixing

**Fig. 1** Electronic contribution from individual orbitals to EFG (DFT/PBE0) for scandium-based molecules. Note: vertical order of orbitals is arbitrary and have no physical significance.**Table 3** The total electric field gradient (in  $E_h/ea_0^2$ ) at Sc in ScF, ScCl, ScBr and ScN at experimental values of the equilibrium bond length

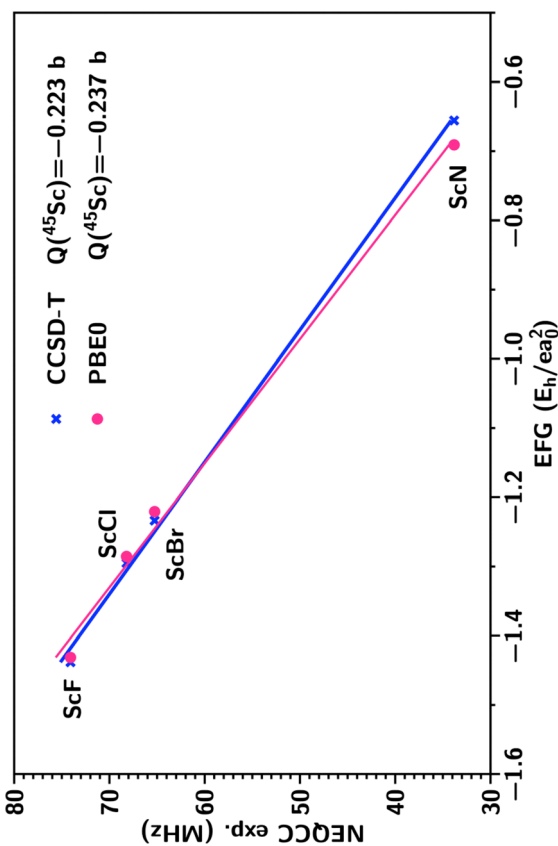
| Method               | ScF     | ScCl    | ScBr    | ScN     |
|----------------------|---------|---------|---------|---------|
| CCSD(T) <sup>2</sup> | -1.451  | -1.315  | -1.258  |         |
| CCSD-T               | -1.4381 | -1.2951 | -1.2335 | -0.6556 |
| DFT/PBE0             | -1.4313 | -1.2854 | -1.2205 | -0.6909 |

between 2p (N) and 3d (Sc). The individual contributions from 2s (N) (negative) and 3p (Sc) (positive) tend to cancel out each other.

The total value of the EFG calculated at the CCSD-T and DFT/PBE0 levels is reported in Table 3 and compared to the reference CCSD(T) values obtained by Kellö *et al.*<sup>2</sup>

These values were used to determine the nuclear electric quadrupole moment of <sup>45</sup>Sc from the curve in Fig. 2.

We observe a very good agreement between the PBE0 functional and the reference CCSD-T results. The NEQM of <sup>45</sup>Sc derived from a linear fit yields a value of -237(9) mb using DFT/PBE0, and -223(3) mb from CCSD(T) calculations, where the uncertainties represent statistical standard errors. These results are consistent with established values reported in prior studies. Kellö *et al.*<sup>2</sup> reported a value of -220(2) mb using a direct evaluation approach for each molecule (ScX X = F, Cl, Br) individually. We propose a new standard value of  $eQ(^{45}\text{Sc}) = -223(3)$  mb.

**Fig. 2** The experimental NEQCC as function of the calculated EFG for scandium-based molecules.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting the conclusions are quoted in the manuscript.

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