

# ХИМИЯ

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*R.A. Ritter, A.V. Fateev, O.Kh. Poleshchuk*

## DENSITY FUNCTIONAL THEORY: ESTIMATION OF NUCLEAR QUADRUPOLE MOMENTS OF SOME NUCLEI

Tomsk State Pedagogical University

Гибридный метод Беке с различными функционалами был использован для расчета констант квадрупольного взаимодействия в большой серии молекул, содержащих 9 различных квадрупольных ядер. Градиенты электрического поля были рассчитаны на основании различных уровней теории: B3LYP/6-31+G(df,pd), B3LYP/cc-pVTZ, BHandHLYP/aug-cc-pVTZ, B3LYP/3-21G(d). Проведена оценка электрических квадрупольных моментов ядер кислорода, фтора, хлора, азота, бора, алюминия, мышьяка, ниобия и сурьмы.

### Introduction

The nuclear quadrupole coupling constant (NQCC) is the spectroscopic measurement of the energy of interaction of the electric quadrupole moment of the nucleus of an atom ( $Q$ ) with the gradient of the molecular electric field (EFG) at the site of the nucleus. If is any significant variation in the electronic structure, as for example in the formation of new chemical bonds, then changes will occur in the EFG's at the quadrupole nuclei, and last will be reflected in their NQCC's. Reliable absolute values of the quadrupole moments  $Q$  are a necessity in any interpretation of experimental data.

Quantum chemistry calculation of the EFG permits calculation of the NQCC, the NQCC being proportional to the EFG. For accurate calculation of the EFG, the need to include electron correlation, along with a fairly basis, is generally conceded. This requirement places severe restrictions on the size of the molecule that may be investigated. Huber et al. [1, p. 168; 2, p. 279; 3, p. 474; 4, p. 279] have shown that the basis need be of high quality principally on and in the area of the nucleus of interest, and that smaller bases may be used on atoms further removed. These authors have applied this method with good results at the level of MP4 to calculation of the EFG's and NQCC's for  $^2\text{H}$ ,  $^{14}\text{N}$ ,  $^{17}\text{O}$  and  $^{33}\text{S}$  nuclei.

Bailey [5, p. 57; 6, p. 195; 7, p. 71; 8, p. 403; 9, p. 318] has shown that results competitive with fourth-order Möller-Plesset perturbation theory can be obtained with much less computational cost using Becke's hybrid Hartree-Fock/Density Functional (HF-DFT) method in conjunction with relatively small Pople type basis, thus enabling calculations on still larger molecules.

Accurate estimates of nuclear quadrupole moments can be obtained by combining experimentally observed nuclear quadrupole coupling constants (NQCC) and

theoretically obtained electric field gradients. We apply this procedure to atoms, where we can use DFT calculations to obtain very accurate electric field gradients (EFG's). By performing sequences we obtain error estimates of the EFG's and nuclear quadrupole moments. The EFG's are very sensitive to core polarization effects. Performing extensive wave function calculations has usually included these effects. In this way, we have produced new estimates of the nuclear quadrupole moments of oxygen, fluorine, chlorine, nitrogen, boron, aluminum, arsenic, niobium and antimony isotopes.

The basis set is large, triple-zeta in the valence space including polarization and diffusion functions except niobium and antimony atoms, and at the Becke's hybrid method with the different correlation functionals [10, p. 5648] achieved within the GAUSSIAN'98 program [11].

### Results and Discussion

We have been used the Microwave spectroscopy data for gaseous molecules (including chlorine, oxygen and nitrogen atoms), time differential perturbed angular distribution measurements for  $^{19}\text{F}^*$  excited state of the fluorine nuclei [12, p. 3398; 13, p. 335; 14, p. 361], nuclear quadrupole resonance for boron, aluminum, arsenic, niobium and antimony nuclei leads to data directly comparable with the present results. In order to determine the quadrupole coupling constants, it has become conventional to (i) assume that the EFG-principal axis lies along the bond axis, and (ii) assume that the asymmetry parameter is zero. Whether these assumptions are reasonable is part of the present study.

The principal components of the EFGs tensors,  $q_{ii}$ , are computed in atomic units (au). In Microwave spectroscopy and nuclear quadrupole resonance, the observable quantity is the so-called quadrupole coupling

tensor  $\chi$ . The two tensorial quantities are related by the following equation:

$$\chi_{ii} [\text{MHz}] = e^2 Q q_{ii} / h = -2.3496 Q [\text{fm}^2] q_{ij} [\text{au}], \quad (1)$$

where  $e$  is the proton electric charge,  $h$  is Planck's constant,  $Q$  is the electric quadrupole moment of the  $^{19}\text{F}^*$ ,  $^{11}\text{B}$ ,  $^{14}\text{N}$ ,  $^{17}\text{O}$ ,  $^{35}\text{Cl}$ ,  $^{27}\text{Al}$ ,  $^{79}\text{As}$ ,  $^{93}\text{Nb}$  and  $^{121}\text{Sb}$  nuclei (in units of  $\text{fm}^2$ ),  $i, j = a, b, c$  (the principle axes of the inertia tensor) or  $x, y, z$  (the principal axes of the NQCC tensor), and the coefficient of 2.3496 arises from the unit conversion.

The proposed calibration procedure consists of three steps. First, one selects a group of small molecules for which accurate values of the QCC's have been determined by high-resolution microwave spectroscopy or nuclear quadrupole resonance. Second, one calculates the EFG values for these small molecules at a particular level of theory. Finally, one adjusts the value of  $Q$  to minimize the errors between the

calculated QCC values and the observed data using eq. 1. Following this procedure, we calibrate the effective  $Q$  of  $^{11}\text{B}$ ,  $^{17}\text{O}$ ,  $^{14}\text{N}$  and  $^{35}\text{Cl}$  at the B3LYP/6-31+G(df,pd) for boron molecules, B3LYP/cc-pVTZ for another light nuclei, BHandHLYP/aug-cc-pVTZ for fluorine molecules, B3PW91/6-311++G(df,pd) of  $^{27}\text{Al}$ ,  $^{75}\text{As}$  and B3LYP/3-21G(d) of  $^{121}\text{Sb}$  and  $^{93}\text{Nb}$  levels. The molecules chosen for initial calibration provide different inequivalent atom sites and represent a variety of  $sp$ ,  $sp^2$ , and  $sp^3$  bond hybridization. The EFG's were calculated on the optimized structures in the same basis set.

Our calculation can produce reliable  $^{11}\text{B}$ ,  $^{17}\text{O}$ ,  $^{14}\text{N}$ ,  $^{19}\text{F}^*$ ,  $^{35}\text{Cl}$ ,  $^{11}\text{Al}$ ,  $^{75}\text{As}$ ,  $^{93}\text{Nb}$  and  $^{121}\text{Sb}$  EFG results when using the effective  $Q(\text{B})$ ,  $Q(\text{O})$ ,  $Q(\text{N})$ ,  $Q(\text{F})$ ,  $Q(\text{Cl})$ ,  $Q(\text{Al})$ ,  $Q(\text{As})$ ,  $Q(\text{Nb})$  and  $Q(\text{Sb})$  of 4.6, 2.45, 2.03, 8.2, 8.24, 20, 37.5, 36 and 70  $\text{fm}^2$ . These values are consistent with the effective  $Q$  values obtained from the experimental data and calibrated at similar levels of theory: (fig. 1-9)

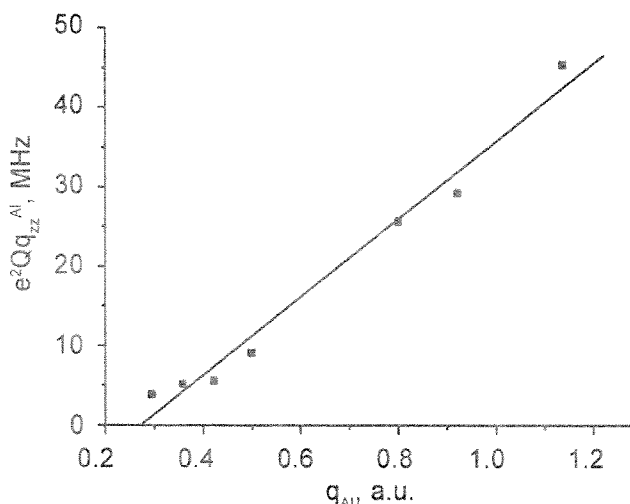


Fig. 1. B3PW91/6-311 + G(df,pd) EFG's versus experimental NQCC's of  $^{27}\text{Al}$  nuclei

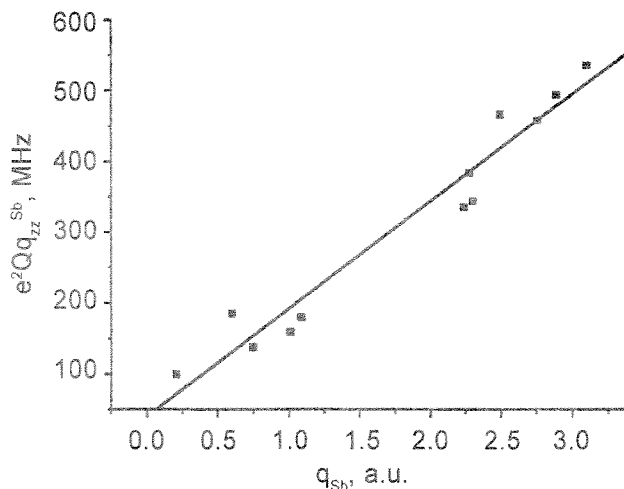


Fig. 2. B3LYP/3-21G(d) EFG's versus experimental NQCC's of  $^{121}\text{Sb}$  nuclei

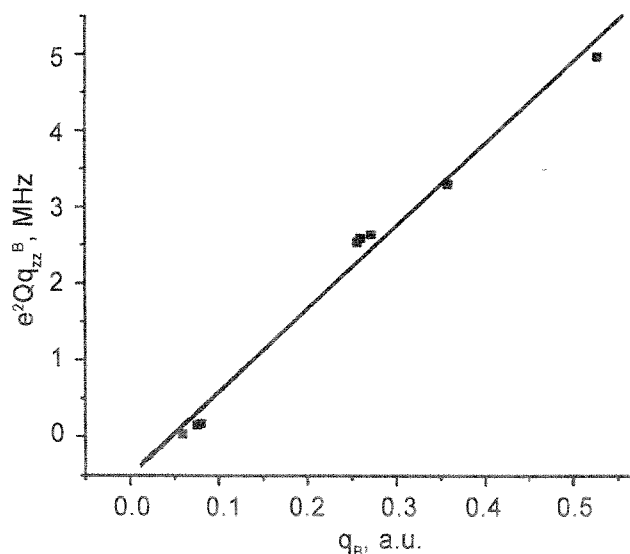


Fig. 3. B3LYP/6-31 + G(df,pd) EFG's versus experimental NQCC's of  $^{11}\text{B}$  nuclei

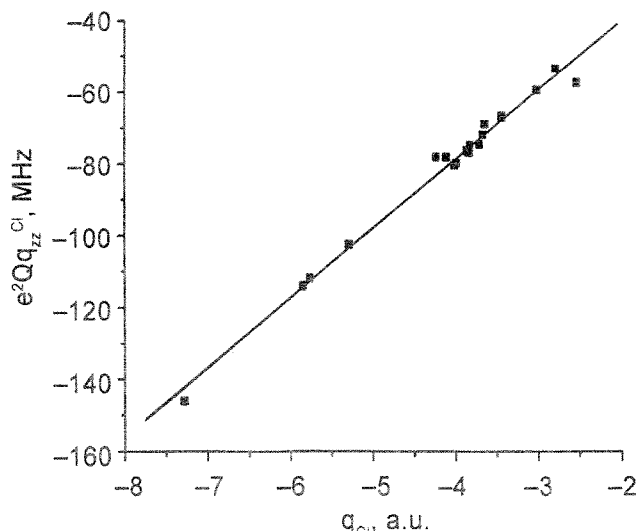


Fig. 4. B3LYP/6-31 + G(df,pd) EFG's versus experimental NQCC's of  $^{35}\text{Cl}$  nuclei

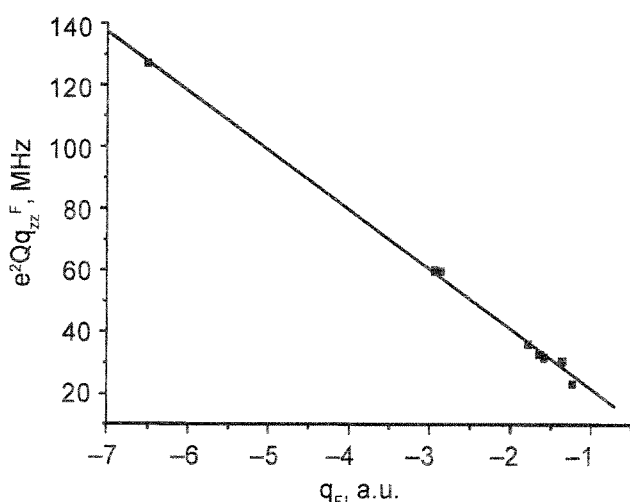


Fig. 5. BHandHLYP/aug-cc-pVTZ EFG's versus experimental NQCC's of  $^{19}\text{F}$  nuclei

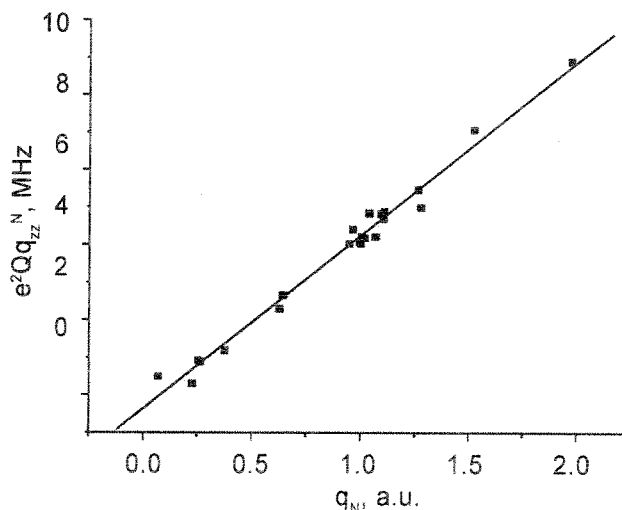


Fig. 6. B3LYP/6-31 + G(df,pd) EFG's versus experimental NQCC's of  $^{14}\text{N}$  nuclei

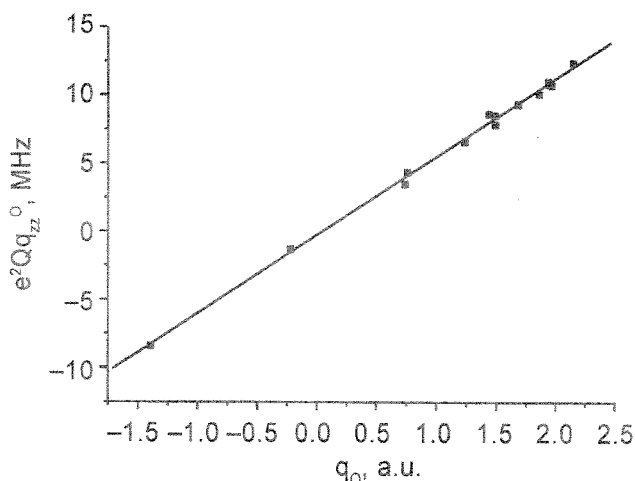


Fig. 7. B3LYP/6-31 + G(df,pd) EFG's versus experimental NQCC's of  $^{17}\text{O}$  nuclei

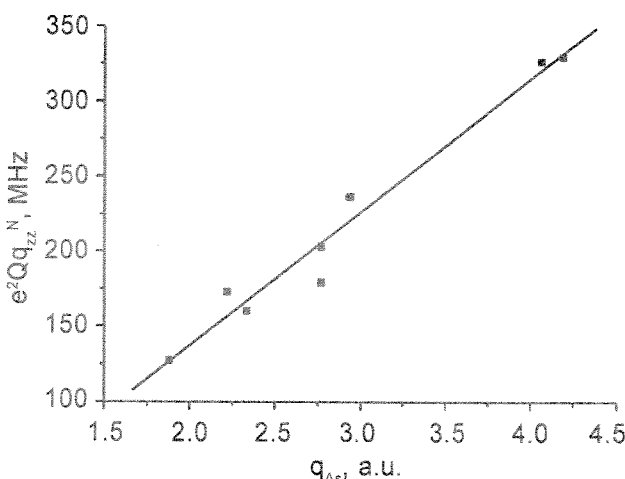


Fig. 8. B3PW91/6-311 + G(df,pd) EFG's versus experimental NQCC's of  $^{75}\text{As}$  nuclei

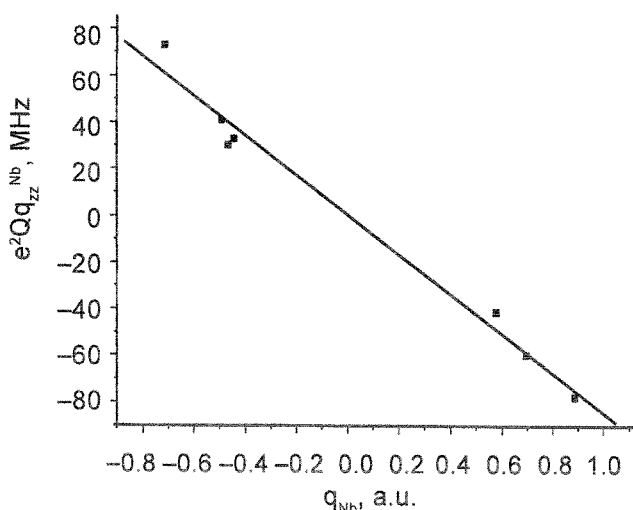


Fig. 9. B3LYP/3-21G(d) EFG's versus experimental NQCC's of  $^{93}\text{Nb}$  nuclei

$Q(\text{B})$ ,  $Q(\text{O})$ ,  $Q(\text{N})$ ,  $Q(\text{F})$ ,  $Q(\text{Cl})$ ,  $Q(\text{Al})$ ,  $Q(\text{As})$ ,  $Q(\text{Nb})$  and  $Q(\text{Sb})$  of 4.06 [15, p. 189]; 2.558 [15, p. 189]; 1.5–2.02 [16, p. 1672; 17, p. 279; 18, p. 3239]; 7.2 [14, p. 361]; 8.249 [16, p. 1672]; 15 [15, p. 189]; 31.4 [16, p. 1672]; 32 [16, p. 1672] and 20–80 fm<sup>2</sup> [19, p. 61]. Using the obtained electric quadrupole moments of some nuclei we found the correlations between calculated and experimental NQCC:

$$e^2Qq_{zz}^{\text{O}}(\text{cal.}) = 0.43 + 1.0 e^2Qq_{zz}^{\text{O}}(\text{exp.})$$

$$(r = 0.997, \text{sd} = 0.4, n = 14); \quad (2)$$

$$e^2Qq_{zz}^{\text{Al}}(\text{cal.}) = 10.3 + 0.6 e^2Qq_{zz}^{\text{Al}}(\text{exp.})$$

$$(r = 0.979, \text{sd} = 2.2, n = 8); \quad (3)$$

$$e^2Qq_{zz}^{\text{B}}(\text{cal.}) = 0.5 + 0.9 e^2Qq_{zz}^{\text{B}}(\text{exp.})$$

$$(r = 0.993, \text{sd} = 0.2, n = 8); \quad (4)$$

$$e^2Qq_{zz}^{\text{F}}(\text{cal.}) = -1.9 + 0.9 e^2Qq_{zz}^{\text{F}}(\text{exp.})$$

$$(r = 0.999, \text{sd} = 1.5, n = 9); \quad (5)$$

$$e^2Qq_{zz}^N(\text{cal.}) = -0.04 + 0.9 e^2Qq_{zz}^N(\text{exp.})$$

( $r = 0.978$ ,  $sd = 0.4$ ,  $n = 21$ );

$$e^2Qq_{zz}^{Cl}(\text{cal.}) = 0.4 + 0.98 e^2Qq_{zz}^O(\text{exp.})$$

( $r = 0.995$ ,  $sd = 2.4$ ,  $n = 18$ );

$$e^2Qq_{zz}^{Sb}(\text{cal.}) = 11 + 0.7 e^2Qq_{zz}^{Sb}(\text{exp.})$$

( $r = 0.991$ ,  $sd = 17$ ,  $n = 9$ );

$$e^2Qq_{zz}^{As}(\text{cal.}) = 36 + 0.8 e^2Qq_{zz}^{As}(\text{exp.})$$

( $r = 0.986$ ,  $sd = 10$ ,  $n = 8$ );

$$e^2Qq_{zz}^{Nb}(\text{cal.}) = 11.2 + 0.34 e^2Qq_{zz}^{Nb}(\text{exp.})$$

( $r = 0.978$ ,  $sd = 2.3$ ,  $n = 8$ ).

Despite of various basis sets we have obtained excellent dependence between calculated and experimental electric quadrupole moments:

$$Q(\text{exp.}) = 0.16 + 0.85Q(\text{cal.})$$

( $r = 0.996$ ,  $sd = 1.1$ ,  $n = 8$ ).

Using this correlation we have estimated the electric quadrupole moment for antimony nucleus as  $59 \text{ fm}^2$  that agree within the limits of experimental accuracy [19, p. 61].

### Conclusions

The Becke3 hybrid model is found to be a viable alternative to the computationally more expensive MP2 or MP4 model for the estimation of all calculated nuclei NQCC's in molecules. Good agreement between the calculated and experimental NQCC's is obtained for all molecular structures optimized with the Becke model. The obtained results have allowed us to estimate of the quadrupole moment of antimony nucleus, for which there are no exact enough experimental data.

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*А.С. Минич\*, И.Б. Минич\*, Н.С. Зеленчукова\*, В.С. Райда\*\*, Г.А. Толстиков\*\*\**

## ВЛИЯНИЕ МЕТЕОРОЛОГИЧЕСКИХ УСЛОВИЙ НА ЭФФЕКТИВНОСТЬ ИСПОЛЬЗОВАНИЯ СВЕТОКОРРЕКТИРУЮЩИХ ПЛЕНОК ДЛЯ ОГРАЖДЕНИЯ ЗАКРЫТОГО ГРУНТА ПРИ ВЫРАЩИВАНИИ РАСТЕНИЙ В УСЛОВИЯХ РЕГИОНА Г. ТОМСКА

\*Томский государственный педагогический университет

\*\*Институт химии нефти СО РАН

\*\*\*Новосибирский институт органической химии

Главным фактором, определяющим стимулирующее влияние светокорректирующих пленок на рост и развитие сельскохозяйственных культур в условиях закрытого грунта («полисветановый» эффект), принято считать в настоящее время наличие под ними фотолюминесцентного излучения красной области

спектра [1, 2]. Наличие такого излучения обеспечивается введением в состав полимерных пленок фотоллюминофоров красного свечения и возбуждением их люминесценции коротковолновым излучением Солнца – прежде всего его УФ-составляющей. Такая роль люминесцентного излучения светокоррек-