

# Density functional theory and Hartree–Fock-density functional theory calculations of $^{17}\text{O}$ , $^{33}\text{S}$ , and $^{73}\text{Ge}$ quadrupole coupling constants

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## Abstract

The performance of several density functional theory and Hartree–Fock density functional theory methods in conjunction with Pople type bases for the calculation of  $^{17}\text{O}$ ,  $^{33}\text{S}$ , and  $^{73}\text{Ge}$  quadrupole coupling constants in gaseous state molecules was investigated.

Assessment of the several models was made by linear regression analysis of the calculated gradient of the molecular electric field versus the experimental nuclear quadrupole coupling constant (NQCCs). Calculations for oxygen on six molecules with the B3LYP/6-311++G(3df,3p) model yield a residual standard deviation of 0.057 MHz (1.4%); for sulfur on 12 molecules with the B3LYP/6-311G(3df,3p) model, 0.42 MHz (1.8%); and for germanium on nine molecules with the B3P86/6-311G(2d) model, 0.83 MHz (1.0%).

In the case of germyl acetylene, our calculations indicate that the experimental NQCC reported some time ago by Thomas and Laurie [J. Chem. Phys. 44 (1966) 2602] was incorrectly assigned with respect to algebraic sign.

Predictions are made of the  $^{17}\text{O}$  and  $^{33}\text{S}$  NQCCs in furan, 4H-pyran-4-one, 4H-pyran-4-thione, and 4H-thiapyran-4-thione; and of the  $^{73}\text{Ge}$  NQCC in germyl bromide. © 2000 Published by Elsevier Science B.V.

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## 1. Introduction

The nuclear quadrupole coupling constant (NQCC) is a spectroscopic measurement of the energy of interaction of the electric quadrupole moment ( $Q$ ) of the nucleus of an atom with the gradient of the molecular electric field (EFG) at the site of the nucleus.

Quantum chemistry calculation of the molecular EFG permits calculation of the NQCC, the NQCC being proportional to the EFG. For accurate calculation of the EFG, the need to include correlation in conjunction with a fairly large basis set is generally acknowledged. This requirement, which is highly demanding on computer resources, places restrictions on the size of the molecule that may be investigated. To overcome these restrictions somewhat, Huber et al. have shown that the basic need be of a high quality principally on and in the area of the atom of interest, and that smaller

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bases may be used on atoms removed further. This method has been applied with good results at the level of fourth-order Møller–Plesset perturbation theory (MP4) to  $^2\text{H}$  [1],  $^{14}\text{N}$  [2],  $^{17}\text{O}$  [3], and  $^{33}\text{S}$  [4].

In a series of recent papers on  $^2\text{H}$  [5],  $^{11}\text{B}$  [6],  $^{14}\text{N}$  [7], and  $^{17}\text{O}$  [8], we have shown that accurate NQCCs may be obtained from EFGs calculated using Becke's [9] hybrid Hartree–Fock density functional theory (HF-DFT) method. The computational efficiency of this method enables calculations on still larger molecules.

As a continuation of these studies, we report the results of our investigation of the efficacy of several density functional theory DFT and HF-DFT methods in conjunction with augmented Pople type 6-311G bases for the calculation of  $^{17}\text{O}$ ,  $^{33}\text{S}$ , and  $^{73}\text{Ge}$  NQCCs in gaseous state molecules. This work represents extension of our investigations to the second and third rows of the periodic table.

Predictions are made of the  $^{17}\text{O}$  and  $^{33}\text{S}$  NQCCs in furan, 4H-pyran-4-one, 4H-pyran-4-thione, and 4H-thiapyran-4-thione; and of the  $^{73}\text{Ge}$  NQCC in germyl bromide.

The method of analysis is discussed in Section 2. The results for oxygen, sulfur, and germanium are reported in Sections 3–5, respectively. Predicted NQCCs in furan and the pyrans are given in Section 6. The results are summarized in Section 7.

## 2. Method

The components of the NQCC tensor,  $\chi_{ij}$ , are related to those of the EFG tensor,  $q_{ij}$ , by

$$\chi_{ij} = (eQ/h)q_{ij}, \quad (1)$$

where  $e$  is the proton electric charge and  $h$  is Planck's constant. The subscripts  $i, j = a, b, c$ ; where  $a, b$ , and  $c$  are the principal axes of the molecular inertia tensor.

The method follows that which was employed previously [5–8]. The coefficient  $eQ/h$  in Eq. (1) is determined by least-squares linear regression analysis of the calculated EFGs versus the experimental NQCCs. Although not independent, all three diagonal components of the EFG tensor are plotted against the corresponding component of

the NQCC tensor. This assures, because the tensors are traceless, that the least-squares line passes through the origin.

The premise that underlies this procedure is that the errors inherent in the level of theory and basis (as well as zero-point vibration and, in the case of Ge, relativistic effects) are systematic and can be corrected, at least partially, by the best-fit coefficient  $eQ/h$ .

Having determined  $eQ/h$ , a model-dependent effective nuclear moment,  $Q_{\text{eff}}$ , may be derived from  $Q_{\text{eff}} = (eQ/h)/234.9649$ , where  $Q_{\text{eff}}$  is in barns (b) and  $eQ/h$  is in MHz/a.u. Since the goal is to accurately reproduce the experimental NQCCs, and not to calculate the nuclear quadrupole moment, the more successful models are those with the smaller residual standard deviations (RSD). It is sufficient that  $Q_{\text{eff}}$  approximate  $Q$  to within several percent.

The DFT methods investigated are Becke's [10] exchange functional in combination with the correlation functionals of Lee et al. (LYP) [11,12], Perdew [13], Perdew and Wang (PW91) [14], and Vosko et al. (VWN5) [15]. These are designated BLYP, BP86, BPW91, and BVWN5, respectively. The HF-DFT methods are Becke's [9] three-parameter method in combination with each of the above cited LYP, P86, and PW91 correlation functionals, respectively, designated B3LYP, B3P86, and B3PW91. Hartree–Fock calculations are included for comparison. All methods were used in conjunction with augmented Pople type 6-311G bases.

The calculations were performed using the GAUSSIAN 94 package of programs [16].

## 3. Oxygen

The performance of the B3LYP/6-311++ G(3df,3p) model for the calculation of  $^{17}\text{O}$  NQCCs was reported in a previous publication [8]. The molecules selected in that work for calibration were  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CO}$ ,  $\text{OCS}$ , and  $\text{HNCO}$ . Here, with the addition of  $\text{CO}_2$  [17], the B3LYP/6-311++ G(3df,3p) model has been recalibrated, and the several DFT and HF-DFT methods cited above have been investigated. Calculations of the

Table 1  
RSD (MHz) of calculated EFG versus experimental NQCC for  $^{14}\text{N}$ ,  $^{17}\text{O}$ ,  $^{33}\text{S}$ , and  $^{73}\text{Ge}$ . Method/6-311++G(3df,3pd)

Method	N <sup>a</sup>	O	S	Ge
HF	0.347	0.169	2.81	9.15
BLYP	0.103	0.079	0.94	2.93
BP86	0.108	0.081	0.89	3.06
BPW91	0.119	0.105	0.90	2.89
BVWN5	0.114	0.138	1.06	2.15
B3LYP	0.045	0.065	0.42	1.59
B3P86	0.034	0.079	0.48	1.48
B3PW91	0.033	0.090	0.50	1.52

<sup>a</sup>Ref. [7].

EFGs were made on the experimental structures. In Table 1, the RSD is given for each of the several methods, all in conjunction with the fully augmented 6-311G basis, i.e., 6-311++G(3df,3pd). The least RSD is obtained with the B3LYP method. Also shown in the table, for comparison, are the corresponding results for  $^{14}\text{N}$  [7], as well as those for sulfur and germanium (see below).

In Table 2, for the B3LYP method, the RSD is given as a function of basis. As was reported in Ref. [8], the best agreement between the calculated and experimental NQCCs is obtained with the B3LYP/6-311++G(3df,3p) model. The addition of  $\text{CO}_2$  does not significantly change the previously reported results. With  $\text{CO}_2$ , the RSD is 0.057 MHz (1.4% of the average absolute experimental

Table 2  
RSD (MHz) of calculated EFG versus experimental NQCC for  $^{17}\text{O}$ . B3LYP/basis

Basis	RSD
6-311++G(3df,3pd)	0.065
6-311+G(3df,3pd)	0.066
6-311G(3df,3pd)	0.135
6-311++G(2df,3pd)	0.101
df	0.073
3d	0.132
2d	0.110
d	0.195
6-311++G(3df,2pd)	0.068
pd	0.072
3p	0.057
2p	0.058
p	0.062
6-311+G(3df)	0.092

NQCC), whereas without, it is 0.056 MHz. With  $\text{CO}_2$ , the best-fit value of  $eQ/h$  is  $-5.840(15)$  MHz/a.u., and without, it is  $-5.834(15)$  MHz/a.u.

The calculated NQCC for  $\text{CO}_2$  is  $-3.83$  MHz, compared with the experimental value of  $-3.92(9)$  MHz. For the other molecules, the calculated NQCCs do not differ appreciably from the values given in Ref. [8].

$Q_{\text{eff}}$  for this model is  $-24.85(6)$  mb, which differs from the recommended value of  $-25.58(22)$  mb [18] by 2.8%.

#### 4. Sulfur

The molecules and experimental  $^{33}\text{S}$  NQCCs [4,19–29] given in Table 3 are those used for calibration of the several computational models. Calculations of the EFGs were made on the experimental structures [30–41]. The calibration results are collected in Tables 1 and 4. The more successful methods, as seen in Table 1, are the B3LYP, B3P86, and B3PW91 hybrids, for which the RSDs are, respectively, 0.42, 0.48, and 0.50 MHz.

In Table 4, for the B3LYP method, the RSD is given as a function of basis. For these calculations, except where noted at the bottom of the table, the default convergence option ( $10^{-4}$  on the root mean square (rms) density) was used. For the three models given at the bottom of the table, the calculations were repeated using the tight convergence option ( $10^{-8}$  on the rms density). For the B3LYP/6-311G(3df,3p) model, e.g., the RSD is the same for both convergence options. However, with the default option,  $eQ/h = -15.51$  MHz/a.u., whereas with the tight option, it is  $-15.58$  MHz/a.u. This difference indicates a difference in the calculated EFGs and suggests that the tight option should be used, but the magnitude of the difference (0.4%) suggests that the convergence need not be tightened further.

Numerical integrations were made over the default grid. This is a pruned (75,302) grid consisting of 75 shells per atom with 302 angular points per shell which, after pruning, results in about 7000 points per atom. Using the B3LYP/6-311G(3df,3p) model with the tight convergence

Table 3  
 $^{33}\text{S}$  quadrupole coupling constants,  $\chi_{ij}$  (MHz), calculated and experimental<sup>a</sup>

Molecule	<i>ij</i>	B3LYP	MP4 <sup>b</sup>	Experimental	Reference
GeS	<i>aa</i>	6.55	6.46	6.85(17)	[19,30]
OCS	<i>aa</i>	-29.52	-30.92	-29.1184(12)	[20,31]
SPF <sub>3</sub>	<i>aa</i>	-29.40	-29.29	-29.924(10)	[21,32]
H <sub>2</sub> S	<i>aa</i>	-33.53	-33.35	-32.820(53)	[22,33]
	<i>bb</i>	-8.02	-7.56	-8.597(66)	
	<i>cc</i>	41.54	40.91	41.416(56)	
SO <sub>2</sub>	<i>aa</i>	-2.22	-1.31	-1.521(95)	[23,34]
	<i>bb</i>	26.59	26.94	25.785(56)	
	<i>cc</i>	-24.36	-25.64	-24.264(105)	
H <sub>2</sub> CS	<i>aa</i>	-12.56	-11.41	-11.898(18)	[24,35]
	<i>bb</i>	50.07	49.57	49.981(12)	
	<i>cc</i>	-37.51	-38.15	-38.083(18)	
Thiirane	<i>aa</i>	-33.46	-32.68	-32.9425(78)	[4,36]
	<i>bb</i>	-16.15	-16.46	-16.402(14)	
	<i>cc</i>	49.62	49.14	49.345(14)	
(CH <sub>3</sub> ) <sub>2</sub> S	<i>aa</i>	-38.44	-38.40	-38.4052(25)	[25,37]
	<i>bb</i>	-9.79	-9.06	-9.7340(31)	
	<i>cc</i>	48.23	47.46	48.1392(36)	
(CH <sub>3</sub> ) <sub>2</sub> SO	<i>aa</i>	-15.58	-16.14	-15.720(18)	[26,38]
	<i>bb</i>	-17.45	-17.80	-17.045(23)	
	<i>cc</i>	33.03	33.94	32.765(25)	
	<i>bc</i>	-2.38	-2.74		
CH <sub>3</sub> SCN	<i>aa</i>	-39.99	-41.01	-40.513(4)	[27,39]
	<i>bb</i>	-7.06	-6.52	-7.166(6)	
	<i>cc</i>	47.05	47.53	47.679(7)	
	<i>ab</i>	4.98	4.65		
Thiophene	<i>aa</i>	7.24	6.73	6.8610(64)	[28,40]
	<i>bb</i>	-27.62	-28.80	-27.8135(63)	
	<i>cc</i>	20.37	22.07	20.9525(47)	
Thiazole	<i>aa</i>	7.58	7.02	7.1708(61)	[29,41]
	<i>bb</i>	-25.96	-27.39	-26.1749(69)	
	<i>cc</i>	18.39	20.36	19.0041(130)	
	<i>ab</i>	-0.81	-1.12		
rms <sup>c</sup>		0.41	0.75		

<sup>a</sup> The first reference is for the experimental NQCC, the second for the molecular structure.

<sup>b</sup> Ref. [4].

<sup>c</sup> The rms difference between calculated and experimental NQCCs. All three diagonal components for all molecules.

option, calculations were made over a finer grid consisting of 99 shells per atom with 434 angular points per shell (99,434), which is 42,966 integration points. The RSD and  $eQ/h$  were found to be the same for both grids. The finer grid appears to be unnecessary.

Fig. 1 is a plot of the calculated EFGs, using the B3LYP/6-311G(3df,3p) model with tight convergence and the default grid, against the experimental NQCCs. The RSD is 0.42 MHz (1.8%), the correlation coefficient is 0.99989, and  $eQ/h$  is -15.578(40) MHz/a.u. The calculated NQCCs are

Table 4  
RSD (MHz) of calculated EFG versus experimental NQCC for  $^{33}\text{S}$  (B3LYP/basis)

Basis	RSD
6-311++G(3df,3pd)	0.42
6-311+G(3df,3pd)	0.42
6-311G(3df,3pd)	0.42
2df	0.46
df	0.71
3d	0.46
2d	0.51
d	0.84
6-311G(3df,2pd)	0.42
pd	0.43
3p	0.42
2p	0.41
p	0.42
6-311G(3df)	0.46
6-311G(3df,3pd) <sup>a</sup>	0.42
3p <sup>a</sup>	0.42
p <sup>a</sup>	0.42

<sup>a</sup> Default integration grid, tight convergence option.

given in Table 3, along with those calculated by Kirchner et al. [4] at the MP4 level, and the experimental values. The rms difference between the

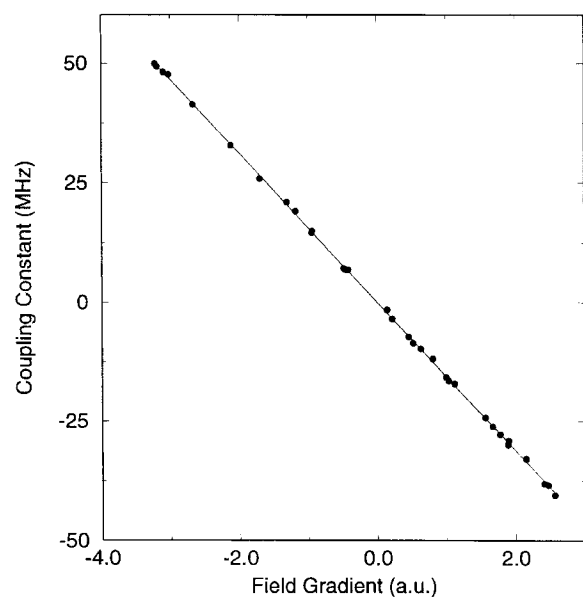


Fig. 1.  $^{33}\text{S}$ : B3LYP/6-311G(3df,3p) calculated EFGs (a.u.) versus experimental NQCCs (MHz). RSD = 0.42 MHz, correlation coefficient = 0.99989,  $eQ/h(\text{slope}) = -15.578(40)$  MHz/a.u.

calculated and experimental NQCCs is 0.41 MHz. For the MP4 calculated NQCCs on these same molecules, the rms difference is 0.75 MHz.

$Q_{\text{eff}}$  for the B3LYP model is  $-66.3(2)$  mb, which differs from the recommended value of  $-67.8(13)$  mb [18] by 2.2%. For the MP4 calculations, the recommended value was used for conversion of the EFGs to NQCCs.

## 5. Germanium

The molecules and experimental  $^{73}\text{Ge}$  NQCCs [19,42–49] given in Table 5 are those used for calibration. Calculations were made on the experimental structures [30,46–48,50–53].

The calibration results are given in Tables 1 and 6. It is seen in Table 1 that the more successful models are the B3LYP, B3P86, and B3PW91 hybrids. The least RSD, namely 1.48 MHz, is obtained with the B3P86 model. With the B3LYP and B3PW91 models, the RSDs are, respectively, 1.59 and 1.52 MHz.

In Table 6, for both the B3PW91 and B3P86 models, the RSD is given as a function of basis. For the B3P86 model, as the basis is reduced from the fully augmented 6-311++G(3df,3pd) to 6-311G(2d,3pd) to 6-311G(2d), the RSD is reduced from 1.48 to 0.90 to its least value of 0.83 MHz. A similar trend is seen for the B3PW91 model. For the B3PW91/6-311G(2d) model, the least RSD is 0.84 MHz.

These calculations were made using the tight convergence option with the (75,302) grid (not pruned), which consists of 22,650 integration points per atom. No significant differences were seen when the integrations were made over a spherical product grid consisting of 96 shells per atom with 32  $\theta$  and 64  $\varphi$  points per shell, which consists of 196,608 integration points per atom. It appears unnecessary to go beyond the (75,302) grid.

Fig. 2 is a plot of the B3P86/6-311G(2d) calculated EFGs versus the experimental NQCCs. The open circle seen in the figure is the reported NQCC of +32.5 MHz for germyl acetylene [47]; the solid circle to which the arrow points is  $-32.5$  MHz. Clearly, the NQCC should be negative, and

Table 5

<sup>73</sup>Ge quadrupole coupling constants  $\chi_{ij}$  (MHz): calculated and experimental<sup>a</sup>

Molecule	<i>ij</i>	Calculated		Experimental	Reference
		B3PW91	B3P86		
GeO	<i>aa</i>	209.3	209.2	208.33(19)	[42,30]
GeS	<i>aa</i>	187.3	187.2	187.785(35)	[19,30]
GeSe	<i>aa</i>	173.9	173.8	172.40(25)	[43,30]
H <sub>3</sub> GeF	<i>aa</i>	-92.2	-92.8	-93.03(10)	[44,50]
H <sub>3</sub> GeCl	<i>aa</i>	-91.9	-92.5	-93.032(15)	[45,51]
H <sub>3</sub> GeBr	<i>aa</i>	-89.2	-89.7		[52] <sup>b</sup>
H <sub>3</sub> GeCCH	<i>aa</i>	-32.8 <sup>c</sup>	-33.2 <sup>c</sup>	32.5 <sup>c</sup>	[46] <sup>d</sup>
H <sub>3</sub> GeCH <sub>3</sub>	<i>aa</i>	2.6	2.4	3.0	[47] <sup>d</sup>
GeF <sub>2</sub>	<i>aa</i>	19.1	19.2	17.2(10)	[48] <sup>d</sup>
	<i>bb</i>	119.4	119.1	121.7(10)	
	<i>cc</i>	-138.5	-138.3	-138.9(10)	
GeH	<i>eq<sub>0</sub>Q</i>	158.9	158.8	158.9(76)	[49,53]

<sup>a</sup> The first reference is for the experimental NQCC, the second is for the structure.<sup>b</sup> For structure.<sup>c</sup> Calculated and experimental NQCC differ with respect to algebraic sign.<sup>d</sup> For the experimental NQCC and for the structure.

Table 6

RSD (MHz) of calculated EFG versus experimental NQCC for <sup>73</sup>Ge (B3PW91/ and B3P86/basis)

Basis	RSD	
	B3PW91	B3P86
6-311++G(3df,3pd)	1.52	1.48
6-311+G(3df,3pd)	1.52	1.48
6-311G(3df,3pd)	1.48	1.43
2df	1.38	1.29
df	1.74	1.54
3d	0.92	0.92
2d	0.87	0.90
d	1.21	1.28
6-311G(2d,2pd)	0.86	0.86
pd	0.86	0.88
3p	0.84	0.87
2p	0.84	0.85
p	0.84	0.88
6-311G(2d)	0.83 <sub>6</sub>	0.83 <sub>2</sub>
6-311G(3d)	0.98	0.92

was assumed negative for the calibration results of Tables 1 and 6. The RSD is 0.83 MHz (1.0%), the correlation coefficient is 0.99997, and  $eQ/h$  is  $-45.317(74)$  MHz/a.u. The calculated NQCCs are compared with the experimental values in Table 5. For germyl bromide, the NQCC given in the table is predicted; no experimental result has been reported.

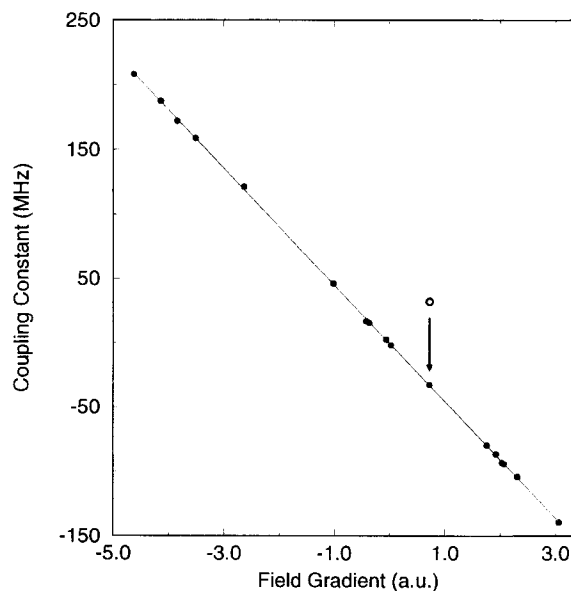


Fig. 2. <sup>73</sup>Ge: B3P86/6-311G(2d) calculated EFGs (a.u.) versus experimental NQCCs (MHz). RSD = 0.83 MHz, correlation coefficient = 0.99997,  $eQ/h(\text{slope}) = -45.317(74)$  MHz/a.u. The open circle is +32.5 MHz for germyl acetylene; the solid circle to which the arrow points is -32.5 MHz.

For the B3PW91/6-311G(2d) model, the RSD is 0.84 MHz, the correlation coefficient is 0.99997, and  $eQ/h = -45.317(74)$  MHz/a.u. For the two methods, B3P86 and B3PW91, the statistics are

essentially the same. In Table 5, the NQCCs calculated with the B3PW91 model are also given, for comparison. Somewhat different results are seen for the two models, particularly for the germyl halides, but the differences are all less than one RSD.

$Q_{\text{eff}}$  derived from  $eQ/h$  is  $-0.1929(3)$  b. Recent large basis set calculations of the EFG at the sites of the  $^{73}\text{Ge}$  nucleus in GeO and GeS have been carried out by Kellö and Sadlej [54] for the purpose of determining the value of the electric quadrupole moment of the nucleus from the known experimental NQCCs. Electron correlation was treated at the level of coupled cluster theory, with corrections for relativistic and zero-point vibrational effects. Their result is  $-0.196$  b. The difference between our  $Q_{\text{eff}}$  and this value is 1.5%. As for the EFGs, the B3P86 model gives for GeO,  $q = -4.616$  a.u. compared with  $-4.543$  a.u. calculated by Kellö and Sadlej; and for GeS,  $-4.130$  a.u. compared with  $-4.064$  a.u. These differences in the EFGs mirror, as expected, the difference between  $Q_{\text{eff}}$  and  $Q$ , and illustrate the premise that underlies the method: namely that the errors are systematic and can be empirically corrected. Note that the factor  $Q_{\text{eff}}/Q$  scales the B3P86 EFGs for GeO and GeS to the more extensively calculated values of Kellö and Sadlej to within less than 0.02%.

## 6. Predicted coupling constants

Predicted NQCCs for  $^{17}\text{O}$  and  $^{33}\text{S}$  in furan, 4H-pyran-4-one, 4H-pyran-4-thione, and 4H-thiapyran-4-thione are given in Table 7. The calculated NQCCs for thiophene are included for comparison. The molecular structure of furan has been determined by Mata et al. [55], the structures of the pyrans by Macdonald et al. [56]. Calculations of the EFGs were made on these structures.

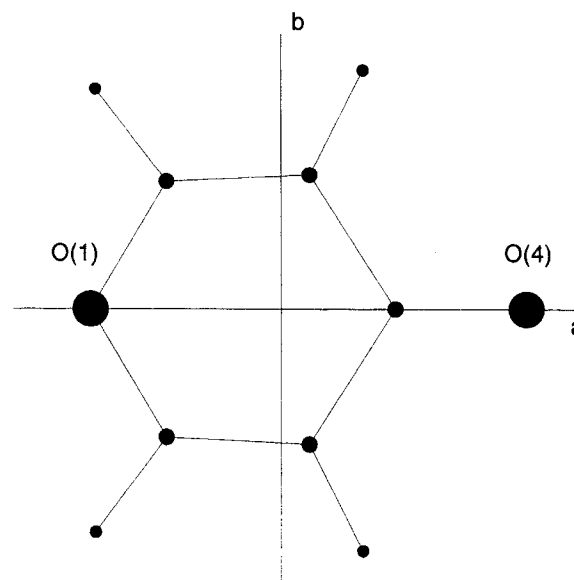


Fig. 3. 4H-pyran-4-one.

4H-pyran-4-one is shown in Fig. 3. In 4H-pyran-4-thione, S(4) is substituted for O(4); in 4H-thiapyran-4-thione, sulfur is substituted for both oxygen atoms.

4H-pyran-4-one is shown in Fig. 3. In 4H-pyran-4-thione, S(4) is substituted for O(4); in 4H-thiapyran-4-thione, sulfur is substituted for both oxygen atoms.

## 7. Summary

The performance of several DFT and HF-DFT methods in conjunction with augmented Pople type bases for the calculation of NQCCs in gaseous state molecules was investigated. Assessment of the several methods was made by linear regression analysis of the calculated EFGs versus the experimental NQCCs. The HF-DFT methods are generally more accurate than the DFT methods, which in turn are more accurate than HF theory.

For  $^{17}\text{O}$  on six molecules, calculations of the EFGs with the B3LYP/6-311++G(3df,3p) model yield a RSD of 0.057 MHz (1.4%); for  $^{33}\text{S}$  on 12

Table 7  
Predicted  $^{17}\text{O}$  and  $^{33}\text{S}$  NQCCs,  $\chi_{ii}$  (MHz)

Molecule	Nucleus	$\chi_{aa}$	$\chi_{bb}$	$\chi_{cc}$
Furan	O(1)	3.87	-7.92	4.05
4H-pyran-4-one	O(1)	3.76	-8.76	5.00
	O(4)	-4.29	10.62	-6.33
4H-pyran-4-thione	O(1)	3.91	-8.58	5.67
	S(4)	-26.34	41.12	-14.78
4H-thiapyran-4-thione	S(1)	3.46	-26.08	22.62
	S(4)	-27.11	43.59	-16.48
Thiophene	S(1)	7.24	-27.62	20.37

molecules with the B3LYP/6-311G(3df,3p) model, 0.42 MHz (1.8%); and for  $^{73}\text{Ge}$  on nine molecules with the B3P86/6-311G(2d) model, 0.83 MHz (1.0%).

The model dependent effective nuclear quadrupole moment  $Q_{\text{eff}}$  for  $^{17}\text{O}$  is  $-24.85(6)$  mb; for  $^{33}\text{S}$ ,  $-66.3(2)$  mb, and for  $^{73}\text{Ge}$ ,  $-0.1929(3)$  b.

In the case of germyl acetylene, our calculations indicate that the experimental coupling constant reported in 1966 by Thomas and Laurie [47] was incorrectly assigned with respect to algebraic sign.

Coupling constants are predicted for  $^{73}\text{Ge}$  in germyl bromide; for  $^{17}\text{O}$  in furan, 4H-pyran-4-one, and 4H-pyran-4-thione; and for  $^{33}\text{S}$  in 4H-pyran-4-thione and 4H-thiapyran-4-thione.

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