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HARTREE-FOCK-SLATER LCAO CALCULATION OF THE MÖSSBAUER PARAMETERS OF SOME ANTIMONY COMPOUNDS

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This paper describes a (non-empirical) Hartree-Fock-Slater ($X\alpha$) LCAO study of the Mössbauer parameters in a series of thirteen Sb compounds: SbX_3 ($X = F, Cl, Br, I$), $Sb(CH_3)_N Cl_{3-N}$ ($N = 1, 2, 3$), SbX_5 ($X = F, Cl$) and $Sb(CH_3)_3X_2$ ($X = F, Cl, Br, I$), in relation with the chemical bonding in these compounds. The calculated isomer shifts agree very well with the experimental data: correlation coefficient 0.99, $\Delta R/R = -1.08 \times 10^{-3}$. The quadrupole splitting for the Sb(III) compounds is consistently (correlation coefficient 0.97) too small by a factor of 2.7, for the Sb(V) compounds the results are more scattered and even smaller. The proportionality factor could be partly due to the uncertainty in the ^{121}Sb nuclear quadrupole moment and partly to the neglect of core polarization effects in the (frozen core) HFS LCAO calculations. Test calculations on HCl, which are also reported in this paper, show that the HFS LCAO method can yield accurate core polarization corrections to the quadrupole splitting (Sternheimer factors), but only at the cost of an expensive numerical integration scheme. The results suggest further that the structures of some of the Sb compounds might be different from what has previously been proposed.

1. Introduction

Since 1960 a large number of Mössbauer spectra have been measured and there has been considerable theoretical effort to calculate the electronic parameters related to these spectra: the electron density and the electric-field gradient (EFG) at the nucleus of the Mössbauer-active atom. Most attempts to rationalize Mössbauer data with quantum-chemical methods have made use of semi-empirical techniques such as the extended Hückel and the CNDO method. More recently the scattered-wave $X\alpha$ method has been applied, mainly to compounds containing Fe [1]. Moreover, there exist also a few (ab initio) Hartree-Fock LCAO treatments of Fe complexes [2] where the Mössbauer parameters are obtained without introducing any empirical data.

As an alternative non-empirical method which yields rather accurate molecular properties and is

cost-effective, so that it can be applied to larger molecules, we consider the Hartree-Fock-Slater LCAO method [3]. It has been used by Geurts et al. [4] to calculate the quadrupole splitting for the complexes $[Fe_4S_4(SH)_4]^{0,2-,3-}$, which model the 4-Fe active site in high-potential iron-protein and ferredoxin; Guenzburger and Ellis [5] applied the closely related HFS discrete variational method (DVM) to calculate the quadrupole splitting and the isomer shift for some linear Au(I) compounds.

The procedure applied by Guenzburger and Ellis [5] differs from the standard HFS DVM method in the numerical integration. They derived a new integration scheme that makes optimum use of the axial symmetry of their compounds and particularly emphasizes the core region. They calculate the EFG by using an analytical procedure for the one-centre terms and a numerical procedure for the two- and three-centre terms.

Geurts et al. [4] employ the standard HFS LCAO method: they calculate the EFG using a STO GTO expansion and a standard molecular properties program, that also calculates the multi-centre contributions to the EFG analytically.

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In this paper we apply the method of Geurts et al. to a group of thirteen antimony compounds, viz. SbX_3 ($X = \text{F, Cl, Br, I}$), $\text{Sb}(\text{CH}_3)_N\text{Cl}_{3-N}$ ($N = 0, 1, 2, 3$), SbX_5 ($X = \text{F, Cl}$) and $\text{Sb}(\text{CH}_3)_3\text{X}_2$ ($X = \text{F, Cl, Br, I}$). Moreover, the calculational procedure was subjected to a more detailed investigation and test on the HCl molecule. Our interest in the Sb compounds was aroused by Stevens and Keijzers [6], who noted a fundamental discrepancy between extended Hückel results for Sb(III) and Sb(V) compounds and the experimental Mössbauer data.

2. Calculational procedures

2.1. The HFS LCAO method

The Hartree–Fock–Slater (HFS) or $X\alpha$ method [7] is characterized by the following one-electron equation:

$$\left(-\frac{1}{2} \nabla^2(1) + \sum_A (-Z_A/r_{A1}) + \frac{1}{2} \int r_{12}^{-1} \rho(2) d\tau_2 - \frac{3}{2} \alpha (3/\pi)^{1/3} [\rho(1)]^{1/3} \right) \phi_\mu(1) = \epsilon_\mu \phi_\mu(1), \quad (1)$$

with the electron density given by

$$\rho(1) = \sum_\mu n_\mu \phi_\mu^*(1) \phi_\mu(1) \quad (2)$$

(we use atomic units unless specified otherwise). In the HFS LCAO method, developed by Baerends et al. [3], eq. (1) is replaced by a secular problem and the matrix elements are (partly) calculated by numerical integration. In several respects, it is similar to the discrete variational method (DVM) introduced by Ellis and Painter [8]. For the further discussion we mention that the point distribution in the numerical integration is given by a superposition of Fermi distributions

$$F(r) = \{1 + \exp[\beta_A(r - r_A)]\}^{-1}, \quad (3)$$

centered at the nuclei A, where β_A and r_A are parameters to be specified; the relative weights of the distributions are given by the fractions f_A of the total number of integration points (N), that are assigned to the nuclei A.

Furthermore, the HFS LCAO method makes use of fit functions for representing the electron density:

$$\rho(1) \approx \sum_i a_i f_i(1), \quad (4)$$

in order to reduce the number of integrals in the calculation of the Coulomb potential:

$$V_C(1) = \sum_i a_i \int r_{12}^{-1} f_i(2) d\tau_2. \quad (5)$$

The coefficients a_i are determined by a least-squares fitting procedure to the “exact” density (2) in any cycle of the iterative (SCF) scheme to solve eq. (1). It is this “exact” density which will be used, after convergence, to calculate the Mössbauer parameters.

We note here that, starting from the $X\alpha$ local exchange approximation, the HFS LCAO method is not subject to any further assumptions with respect to the form of the potential. In particular, one does not use the (rather crude) muffin-tin approximation employed in the multiple-scattering $X\alpha$ method [9]. It has been demonstrated [10] that it is a very useful tool for rather accurate calculations of various molecular properties.

2.2. Mössbauer parameters

The two parameters describing Mössbauer spectra are the isomer shift (IS) and the quadrupole splitting (QS). These quantities are directly related to the electron distribution in the molecular system; the IS to the electron density, the QS to the EFG, both at the nucleus of the Mössbauer-active atom [11,12].

The IS δ is given by the following first-order perturbation expression:

$$\delta = \frac{4}{5} \pi Z R^2 (\Delta R/R) S'(S) [\rho_A(0) - \rho_S(0)], \quad (6)$$

where Z is the nuclear charge, R the nuclear radius, ΔR its increase upon excitation and $S'(Z)$ a dimensionless quantity correcting for relativistic effects (e.g., for Sb with $Z = 51$, $S' = 2.38$ [12]); the subscripts S and A refer to source and absorber, respectively. In an LCAO calculation the density (2) at the nucleus follows from

$$\rho(0) = \sum_\mu n_\mu \sum_{p,q} C_{p\mu}^* C_{q\mu} \chi_p^*(0) \chi_q(0), \quad (7)$$

where $\{\chi_p\}$ denotes the set of AOs and the $C_{p\mu}$ are expansion coefficients. In semi-empirical calculations one calculates the contribution from the valence orbitals as

$$\rho_{\text{val}}(0) = N_{\text{val},s}(1 - \beta)|\chi_{\text{val},s}(0)|^2, \quad (8)$$

where $N_{\text{val},s}$ is the (Mulliken) net atomic population ($\sum_{\mu} n_{\mu} C_{p\mu}^2$) of the s-type valence orbital and $(1 - \beta)$ is a screening factor [13].

The electrostatic quadrupole interaction between the asymmetric nuclear charge distribution, described by the nuclear quadrupole moment Q , and an inhomogeneous electric field, described by the EFG tensor \mathbf{V} , gives rise to a splitting of the nuclear energy levels [11]:

$$E_Q = [V_{zz}Q/4I(2I - 1)][3m_I^2 - I(I + 1)] \times (1 + \frac{1}{3}\eta^2)^{1/2}, \quad (9)$$

where I is the nuclear spin ($> \frac{1}{2}$), m_I its z component, V_{zz} the dominant element of the diagonalized EFG tensor and $\eta = |(V_{xx} - V_{yy})/V_{zz}|$ the asymmetry parameter.

The elements of the EFG tensor are calculated as a sum of nuclear and electronic contributions:

$$V_{ij} = V_{ij}^{\text{nuc}} + V_{ij}^{\text{el}}, \quad i, j = \{x, y, z\},$$

$$V_{ij}^{\text{nuc}} = \sum_B Z_B (3R_{Bi}R_{Bj} - \delta_{ij}R_B^2)/R_B^5,$$

$$V_{ij}^{\text{el}} = -\langle \Phi | \sum_k (3r_{ki}r_{kj} - \delta_{ij}r_k^2)/r_k^5 | \Phi \rangle. \quad (10)$$

In a LCAO calculation the electronic contribution to the EFG can be separated into one-, two- and three-centre terms. Denoting the Mössbauer-active nucleus as A (all coordinates \mathbf{R}_B and \mathbf{r}_k are measured with respect to this nucleus), the other nuclei as B, C, one obtains:

$$V_{ij}^{\text{el}} = V_{ij}^{\text{el},1} + V_{ij}^{\text{el},2} + V_{ij}^{\text{el},3},$$

$$V_{ij}^{\text{el},1} = \sum_{\mu} n_{\mu} \sum_{a', a''}^A C_{a'\mu}^* C_{a''\mu} \times \langle \chi_{a'} | (3r_i r_j - \delta_{ij} r^2)/r^5 | \chi_{a''} \rangle,$$

$$V_{ij}^{\text{el},2} = 2 \sum_{\mu} n_{\mu} \sum_a^A \sum_{b \in B(\neq A)}^B C_{a\mu}^* C_{b\mu}$$

$$\times \langle \chi_a | (3r_i r_j - \delta_{ij} r^2)/r^5 | \chi_b \rangle$$

$$+ \sum_{\mu} n_{\mu} \sum_B \sum_{b', b''}^B C_{b'\mu}^* C_{b''\mu}$$

$$\times \langle \chi_{b'} | (3r_i r_j - \delta_{ij} r^2)/r^5 | \chi_{b''} \rangle,$$

$$V_{ij}^{\text{el},3} = \sum_{\mu} n_{\mu} \sum_{B(\neq A)}^B \sum_b^B \sum_{C(\neq A, B)}^C C_{b\mu}^* C_{c\mu}$$

$$\times \langle \chi_b | (3r_i r_j - \delta_{ij} r^2)/r^5 | \chi_c \rangle. \quad (11)$$

In practice one often neglects the three-centre terms and assumes that the two-centre terms cancel the nuclear contribution, thus retaining the one-centre electronic terms only [14].

In semi-empirical calculations on systems with p-type valence shells one uses the Townes-Dailey equation [15], which reads

$$V_{zz} = \langle r^{-3} \rangle_p (N_{p_z} - \frac{1}{2}N_{p_x} - \frac{1}{2}N_{p_y})(1 - R). \quad (12)$$

Here $\langle r^{-3} \rangle_p$ is the expectation value over the p valence orbital in the free atom, the N s are net atomic orbital populations and $(1 - R)$ is the Sternheimer correction discussed in section 2.3.

2.3. Frozen-core calculations: the Sternheimer effect

In molecular calculations one often uses the frozen-core approximation, assuming that the cores of the atoms in a molecular system are unaffected by the chemical bonding. Since in such a treatment the cores stay spherically symmetric, the core of the Mössbauer-active atom gives a constant contribution to the density at the nucleus $\rho(0)$ and a zero contribution to the EFG.

This approximation seems to work reasonably well for $\rho(0)$, differences in $\rho(0)$ for inner core orbitals are shown to be very small for free atoms in different oxidation states [2,16]. For outer core orbitals the situation is somewhat less clear-cut [2,16]. For the EFG, however, the approximation breaks down: the core electrons are polarized by the distorted valence-electron distribution and the field due to the nuclei and the cores of the other atoms in the system. The distortion is small, but it is amplified by the large values for $\langle r^{-3} \rangle$ in the calculation of the EFG tensor. This core polariza-

tion or Sternheimer shielding [17] is allowed for in frozen-core calculations by the use of the Sternheimer factor R :

$$V_{zz}^{\text{observed}} = (1 - R)V_{zz}^{\text{valence}}. \quad (13)$$

More correctly one uses a Sternheimer factor R^{ab} for every orbital pair (a, b). It is to be noted, however, that the use of Sternheimer factors corrects for approximations in the MO calculation. In an all-electron calculation the core polarization is taken into account in a self-consistent manner and there is no need to use Sternheimer factors to correlate the results with experiment.

One has tried to calculate Sternheimer factors from atomic models [17,18]. The use of such correction factors in molecular calculations should, for various reasons, be regarded with scepticism.

2.4. Computational procedure

We have used the HFS LCAO program of Baerends et al. [19], adapted to IBM. In all our calculations we have taken the exchange parameter α fixed at 0.7 [3]. For fitting the electron density (4) we took a subset of all products of the STO basis functions on the atomic centres.

The density at the nucleus of the Mössbauer-active centre may easily be obtained from the converged charge-and-bond-order matrix of the SCF calculation.

The EFG was calculated using the one-electron properties package of the POLYATOM program [20], which is based on GTOs. This properties package calculates all multicentre terms, so that we could check approximations made with respect to two- and three-centre terms.

Further we have used an interface program that reads the converged SCF data from the HFS LCAO program, expands the STOs in GTOs and prepares the input for the properties package. The STO GTO expansion is performed according to the method of maximum overlap fits of Stewart [21]. Each (n, l) STO is expanded in a number of ($l+1, l$) GTOs, i.e. s-type STOs in 1s GTOs, p-type STOs in 2p GTOs, etc. The number of GTOs may vary between 1 and 6.

3. Test calculations on HCl

We have chosen the HCl molecule to perform some test calculations because it is sufficiently small to investigate the influence of all relevant parameters and there are extensive data available in the literature allowing us to check our results. All our calculations were performed for HCl at the equilibrium geometry ($R = 2.4086$ bohr), which has an experimental EFG at the chlorine nucleus $q_{\text{exp}} = -3.641$ au (calculated from $e^2qQ = 67.0 \pm 0.6$ MHz and $Q = -0.0782$ barn [22]); hence the electronic contribution $q_{\text{exp}}^{\text{el}} = -3.498$ au.

The nine occupied MOs in HCl can be subdivided into two sets: on the one hand, $1\sigma, 2\sigma, 3\sigma, 1\pi_x$ and $1\pi_y$, which have mainly Cl core character and on the other hand, the occupied combinations of $3s^{\text{Cl}}, 3p_z^{\text{Cl}}$ and $1s^{\text{H}}$: 4σ and 5σ , and the non-bonding $2\pi_x$ and $2\pi_y$ (the molecule is taken along the z axis). In the calculation of the EFG we make

Table 1
STO basis sets used for HCl

Orbital	Exponent		
		Cade-Huo [23] like ^{a)}	HFS TZ [29]
Cl	1s	18.673	13.95
	2s	16.428	5.65
		5.794	
	3s	10.116	3.30
		2.792	2.30
		1.715	1.60
	2p	14.021	6.70
		8.325	
		5.267	
	3p	2.514	2.85
1.389		2.05	
		1.20	
3d	2.40	2.40	
H	1s	1.508	
		2.568	
	2s	2.270	
	2p	1.763	

^{a)} The 3d polarization function for H has been omitted; unlike Cade and Huo we take the same exponents for the σ and π basis.

Table 2
EFG and $\rho(0)$ (in au) for HCl

	q^{core}	q^{val}	q^{el}	$10^3\rho(0)$
HFS LCAO; all electron ^{a)}				
$N = 800$	-3.481	-3.577	-7.038	3.1096
$N = 2500$	1.070	-3.150	-2.080	3.1654
$N = 5000$	0.148	-3.090	-2.942	3.2134
$N = 10000$	0.088	-3.055	-2.967	3.2028
$N = 15000$	-0.079	-3.058	-3.136	3.1962
$N = 20000$	-0.046	-3.072	-3.118	3.1974
$N = 25000$	-0.181	-3.092	-3.273	3.1978
$N = 30000$	-0.156	-3.082	-3.238	3.1978
HFS LCAO; frozen core ^{b)}				
$r_{\text{Cl}} = 2.0, \beta_{\text{Cl}} = 1.0$			-2.763	
$r_{\text{Cl}} = 1.44, \beta_{\text{Cl}} = 1.2$			-2.755	
$r_{\text{Cl}} = 1.0, \beta_{\text{Cl}} = 1.2$			-2.769	
$r_{\text{Cl}} = 1.44, \beta_{\text{Cl}} = 1.5$			-2.718	
Petke and Whitten [25]	-0.221	-3.687	-3.898	
Scrocco and Tomasi [26]	-0.642	-3.147	-3.789	
Moccia ^{c)}	-0.886	-2.846	-3.733	
McLean and Yoshimine [22]	-0.451	-2.952	-3.403	
Cade and Huo [23]	-0.518	-2.959	-3.478	
Grabenstetter and Whitehead [27]	-0.539	-2.955	-3.494	
experiment [2]			-3.498	

^{a)} Using the Cade-Huo like basis of table 1. Other integration parameters fixed at $f_{\text{Cl}} = 0.8, r_{\text{Cl}} = 1.449, \beta_{\text{Cl}} = 1.389; f_{\text{H}} = 0.2, r_{\text{H}} = 0.507, \beta_{\text{H}} = 1.508$.

^{b)} Using the HFS TZ basis of table 1. Other integration parameters fixed at $N = 1000; f_{\text{Cl}} = 0.8; f_{\text{H}} = 0.2, r_{\text{H}} = 0.564, \beta_{\text{H}} = 1.508$. See also text.

^{c)} Calculated by Grabenstetter and Whitehead [27] from the MOs given by Moccia [28].

the corresponding separation:

$$q^{\text{el}} = q^{\text{core}} + q^{\text{val}}. \quad (14)$$

In the HFS calculations the fractions of the integration points per centre were taken as $f_{\text{Cl}} = 4/5, f_{\text{H}} = 1/5$ throughout. Convergence of the SCF procedure was achieved to 3×10^{-6} for the mean change in the diagonal elements of the charge-and-bond-order matrix. For the calculation of the EFG we used an expansion of all STOs in six GTOs [4].

In the first place we performed all-electron calculations with a basis set derived from the one used by Cade and Huo [23], see table 1. We used a density fit set containing 9 s, 7 p and 5 d functions on Cl and 3 s and 1 p functions on H. Inclusion of some additional f- and g-type fit functions had no effect on the calculated EFG. Varying the integration parameters r_{A} and β_{A} (3) for the usual num-

bers of integration points ($N = 1000-2500$) we found the EFG to be extremely sensitive, much more so than the one-electron eigenvalues. This is not surprising since the HFS LCAO method has been developed for valence-electron properties, which is reflected in the use of the Fermi distribution that emphasizes the valence region. For the EFG the core region should also be very accurately described (due to the $\langle r^{-3} \rangle$ weighting).

This sensitivity with respect to the integration parameters has led us to examine the influence of increasing the number of integration points beyond the limits normally used. From table 2 one can clearly see that the instability in the EFG is mainly due to the core contribution, which is not quite stable yet at $N = 15000$. It can also be seen from table 2 that the density at the nucleus is much more well-behaved.

Comparing with the EFG calculations from the

Table 3
Comparison of some properties (in au) of HCl between the present HFS calculation and the literature

Property ^{a)}	McLean and Yoshimine (HF LCAO) [22]	HFS LCAO ^{b)}	Difference (%)
$\langle r_1^{-1} \rangle$	64.822	64.380	0.7
$\langle r_2^{-1} \rangle$	8.001	7.987	0.2
$\langle z_1 \rangle$	1.931	1.881	2.6
$\langle z_1^2 \rangle$	13.389	13.384	0.03
$\langle x_1^2 + y_1^2 \rangle$	20.871	20.861	0.05
$\langle r_1^2 \rangle$	34.260	34.245	0.04
$\langle z_1 r_1^{-3} \rangle$	0.168	0.139	21.1
$\langle z_2 r_2^{-3} \rangle$	-2.939	-2.911	1.0
$\langle (3z_1^2 - r_1^2)r_1^{-5} \rangle$	-3.419	-3.238	5.6
$\langle (3z_2^2 - r_2^2)r_2^{-5} \rangle$	2.153	2.115	1.8

^{a)} Indices 1 and 2 refer to Cl and H as origins, respectively.

^{b)} All-electron HFS LCAO calculation with $N = 30000$ (see table 2).

literature it is observed that the core contribution is the more variable one also in general. The difference between the various results can be largely ascribed to this contribution. We note that there is reasonable agreement between the HFS LCAO calculation and other (ab initio HF LCAO) calculations.

In table 3 we compare some other properties of HCl with McLean and Yoshimine's HF LCAO results [22] (obtained with Cade and Huo's basis [23] extended with another 12 STOs). For the positive moments of the electron density the agreement is quite good, whereas for the negative moments it is only satisfactory. Again, this reflects the valence electron directed character of the HFS LCAO method.

Just as Guenzburger and Ellis [5] we tried to increase the stability of the all-electron calculation by changing the point distribution in the numerical integration, especially to improve the core description. Guenzburger and Ellis performed the angular integration by imposing the axial symmetry of their molecules on the electron density. In their calculations they still needed 29000 integration points to obtain core contributions stable to six decimal figures. Since the antimony compounds we are interested in are non-linear, we tried a different approach. First we followed a suggestion of Ellis [24] to use a superposition of two Fermi distributions centered at the Cl nucleus,

secondly we changed the Fermi distribution into an exponential distribution. It turned out that for equal numbers of integration points, no substantial improvement over the usual procedure was obtained. This indicates that the essential feature of the method employed by Guenzburger and Ellis is the full use of the $C_{\infty v}$ or $D_{\infty h}$ symmetry.

Beside the all-electron calculations we also performed frozen-core calculations with the 1s, 2s and 2p orbitals as Cl core. We used the HFS TZ basis [29], listed in table 1, for Cl and a Cade-Huo like basis set for H. As expected from the preceding results, the calculated EFG appeared to be much more stable with respect to variations in the integration parameters than for the all-electron case (see table 2; the variation in q^{el} over the same range of integration parameters amounts to as much as 2.7 au in the all-electron calculations). Because the core is frozen now, we neglect the core polarization; the overall Sternheimer factor is found to be $1 - R = 1.18$ for HCl.

Finally, we varied the size of the Cl core. It turned out that instabilities in the EFG arose as soon as the Cl 2p orbital was included in the valence set.

We conclude that it is possible to obtain stable EFGs within the HFS LCAO method either by performing all-electron calculations with very large numbers of integration points or by performing frozen-core calculations with a standard choice of integration parameters. Calculations of the first kind are rather expensive and, so, they are not very advantageous with respect to ab initio quantum-chemical methods. For many problems of chemical interest the first option may be impractical, however. If one is interested in relative changes of Mössbauer parameters among series of similar compounds (where the Sternheimer factor may be assumed constant) the HFS LCAO frozen-core method forms a more reliable alternative for the often used semi-empirical methods.

4. Calculations on antimony compounds

4.1. Available Mössbauer data

Mössbauer data are known on many antimony compounds; a thorough theoretical explanation of

Table 4
Experimental Mössbauer parameters ^{a)}

Molecule	δ (mm s ⁻¹) (relative to InSb)	e^2qQ (mm s ⁻¹)	η	Ref.
SbF ₃	-5.97	19.7		[38]
	-6.0	19.6		[39]
	-6.04 ^{b)}	19.6		[40]
	-6.29 ^{c)}	19.1		[41]
SbCl ₃	-5.24 ^{b)}	12.2		[40]
	-5.77 ^{d)}	12.2	0.19	[42]
	-5.87 ^{c)}	12.25	0.187	[44]
	-5.9	13.2	0.2	[43]
	-5.9	13.9		[45]
	-6.94 ^{b)}			[46]
SbBr ₃	-5.87 ^{d)}	11.6	0.1	[42]
	-5.9	11.6		[45]
	-5.9	10.7	0.3	[43]
	-5.92 ^{c)}	11.6	0.39	[44]
	-6.94 ^{b)}			[46]
	-7.24 ^{b)}			[47]
SbI ₃	-7.34 ^{b)}			[40]
	-7.67 ^{d)}	5.6		[42]
	-7.7			[43]
	-7.74 ^{b)}			[47]
	-7.94 ^{b)}			[46]
				[48]
SbF ₅	10.2	8.7		[53]
	10.3	8.7		[54]
	10.79 ^{b)}			[40]
SbCl ₅	5.06 ^{b)}			[55,56]
	5.2	-5.7		[53,54]
	5.44 ^{b)}	-4.4		[40]
SbMeCl ₂	-4.2	31.0	0.35	[31]
	-4.37	30.0		[42]
SbMe ₂ Cl	-2.5	31.7	0.77	[31]
	-2.6	30.0	0.82	[31]
	-3.07 ^{d)}	-26.0	0.9	[42]
	0.00 ^{d)}	15.2		[42]
SbMe ₃	-0.22	16.3		[48]
	2.42 ^{d)}	-24.0		[49,50]
	2.49	-24.0		[51]
SbMe ₃ Cl ₂	2.86 ^{b)}	-24		[50]
	2.13 ^{d)}	-22.1		[49,50]
	2.20	-22.1		[51]
	2.38 ^{c)}	+21.43		[52]
	2.38 ^{c)}	+20.9		[52]
SbMe ₃ Br ₂	2.56 ^{b)}	-22		[51]
	2.16	-19.28		[51]
				[51]
				[51]
				[51]

^{a)} Experimental data of SbMe₃F₂ unknown.^{b)} Measured with SnO₂ as source.^{c)} Measured with BaSnO₃ as source.^{d)} Measured with CaSnO₃ as source.

the parameters in terms of electronic quantities is still lacking, however. The discussions of Sb compounds are either based on simple qualitative models [30,31] or on semi-empirical calculations [13,32–34]. Usually one treats a series of related compounds, in order to study the effect of substitution of one or more organic by inorganic ligands. One such series is $\text{Sb}(\text{CH}_3)_N \text{Cl}_{3-N}$ ($N = 0, 1, 2, 3$) for which Stevens et al. [31] gave a qualitative explanation of the IS and the QS as a function of N . Stevens et al. also performed extended Hückel calculations and they found the size of the QS to agree reasonably well with experiment. For some Sb(V) compounds, however, the method failed: the calculated QS was a factor of 10 too small compared with experiment [6].

Here we consider four series of antimony compounds: two containing Sb(III), viz. SbX_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and $\text{Sb}(\text{CH}_3)_N \text{Cl}_{3-N}$ ($N = 0, 1, 2, 3$) and two containing Sb(V), viz. SbX_5 ($X = \text{F}, \text{Cl}$) and $\text{Sb}(\text{CH}_3)_3 \text{X}_2$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). In table 4 we present a survey of the experimental Mössbauer data on these molecules. In order to facilitate comparison of the numbers, we have shifted all isomer-shift data relative to InSb. We used the following isomer shifts for InSb with respect to

various sources: $\delta = -8.53 \text{ mm s}^{-1}$ for CaSnO_3 [35], $\delta = -8.5 \text{ mm s}^{-1}$ for BaSnO_3 [36] and $\delta = -8.56 \text{ mm s}^{-1}$ for SnO_2 [37].

Regarding the QS, we wish to make a special comment on the sign. The fit procedure used to determine the Mössbauer parameters from experimental spectra is sensitive to the magnitude of the QS, but not very sensitive to its sign. For SbMe_3Br_2 we found contradictory data; looking at the other two compounds from the series SbMe_3X_2 we think it likely that the sign should be negative (which is confirmed by our calculations, see below). For SbMe_2Cl both the available references give a negative sign for the QS. Still we think it probable that the sign is positive since it is unlikely that in the series $\text{SbMeCl}_2\text{--SbMe}_2\text{Cl--SbMe}_3$ the QS will change sign twice upon substitution. Again, this will be confirmed by our calculations.

4.2. Calculations

Table 5 lists the geometries of the molecules used in our calculations. We have assumed C_{3v} point group symmetry for all molecules except $\text{Sb}(\text{CH}_3)_2\text{Cl}$ and $\text{Sb}(\text{CH}_3)\text{Cl}_2$, for which we adopted C_s point group symmetry. By conse-

Table 5
Geometries used for the antimony compounds ^{a)}

Molecule	Ref.	Distances (Å)		Angles (deg)		
		Sb–X	Sb–C	X–Sb–X	X–Sb–C	C–Sb–C
SbF_3	[31]	2.00	–	81.9	–	–
SbCl_3	[57]	2.360	–	95.2	–	–
SbBr_3	[58]	2.51	–	97	–	–
SbI_3 A	[59]	2.67	–	99	–	–
SbI_3 B	[31]	2.87	–	95.8	–	–
SbMeCl_2	[31]	2.355	2.132	95.2	97	–
SbMe_2Cl	[31]	2.355	2.132	–	97	105
SbMe_3	[31]	–	2.132	–	–	98
SbF_5	[13]	eq. 2.00 ax. 2.13	–	180 and 120	–	–
SbCl_5	[60]	eq. 2.29 ax. 2.34	–	180 and 120	–	–
SbMe_3F_2	[61]	2.091	1.997	180	90	120
SbMe_3Cl_2	[62,63]	2.355	2.132	180	90	120
SbMe_3Br_2	[62]	2.471	2.143	180	90	120
SbMe_3I_2	[62]	2.609	2.164	180	90	120

^{a)} C–H = 1.091 Å and $\angle\text{H–C–H} = 95.2^\circ$ throughout.

Table 6
Exponents of STO basis sets used in the calculations (in au) [29]

	H	C	F	Cl	Br	I	Sb
1s	1.383 0.783	5.40	8.33	14.55	23.90	36.40	36.65
2s		1.98 1.24	3.32 1.92	5.60	13.75	19.40	18.20
2p		2.20 0.96	3.52 1.48	6.65	14.50	24.85	24.75
3s				2.90 1.75	7.05	11.95	11.45
3p				2.45 1.30	7.35	10.50	8.95
3d					5.34	11.60	10.94
4s					3.25 1.95	6.90	6.55
4p					2.65 1.40	7.10	7.10
4d						4.69	5.45 3.05
5s						3.20 1.95	2.85 1.70
5p						2.65 1.45	2.25 1.20

quence, the asymmetry parameter η can be non-zero for the latter two molecules only. In establishing the geometries we made use of X-ray data as much as possible.

For the series SbX_3 we took the angles and distances mentioned by Bowen et al. [37], for SbI_3 we also used the geometry proposed by Wells [59] (structure A). The angles in the series $\text{Sb}(\text{CH}_3)_N\text{Cl}_{3-N}$ are those suggested by Stevens et al. [31], the distances were estimated. The structures of SbF_5 and SbCl_5 are rather uncertain [37]; one has assumed a pure trigonal bipyramid, but also a deformed octaeder has been proposed. For SbF_5 we used Kothekar's geometry [13], for SbCl_5 Polynova's [60] which also has been adopted by Baltranas et al. [34]. We also tried to find structural data on SbBr_5 and SbI_5 ; since we did not succeed, we omitted them from our calculations. The series $\text{Sb}(\text{CH}_3)_3\text{X}_2$, finally, has a trigonal bipyramidal structure with the methyl groups in the equatorial positions [62]. For $\text{X} = \text{F}$ the X-ray data are known [61]. The $\text{Sb}-\text{Cl}$ distance was taken as in $[\text{Sb}(\text{CH}_3)_2\text{Cl}_3]_2$ [63]. The $\text{Sb}-\text{Br}$ distance used is an average of some distances known from X-ray diffraction; the $\text{Sb}-\text{I}$ distance was estimated.

We performed frozen-core HFS LCAO calculations with the exchange parameter $\alpha = 0.7$ throughout [3]. The cores taken are 1s for C and F, 1s-2p for Cl, 1s-3d for Br, 1s-4d for I and 1s-4p for Sb, so for Sb the 4d was included in the valence set. The basis sets employed [29] are listed in table 6. They are of double-zeta type for the valence orbitals, supplemented with single-zeta core functions to allow for core orthogonalization. In the density-fit procedure we gave special attention to the Sb atom; for Sb we used a fit set consisting of 12 s, 7 p, 6 d, 3 f and 2 g Slater-type functions. The number of integration points used was 2000 for Sb, 600 for halogens, 400 for C and 200 for H. Convergence in the SCF procedure was obtained to 3×10^{-5} for the mean change in the diagonal elements of the charge-and-bond-order matrix.

In the calculation of the EFG the STOs centered on Sb were expanded in five GTOs and those on other atoms in four GTOs, which gives an error of less than 0.01 au in the calculated EFG due to the STO GTO expansion.

We have checked that the Sb core was sufficiently large for the EFG to be stable with respect

to variations in the integration parameters used in the HFS calculation (cf. section 3). It turned out that the core taken constitutes the "minimum choice", i.e. inclusion of the 4p orbitals in the valence set causes instabilities under normal integration conditions.

4.3. Results and discussion

Tables 7 and 8 and fig. 1 summarize our results. Table 7 contains the Mulliken gross and net populations of the valence orbitals on Sb. First we note that the gross populations of the 4d orbitals stay practically constant at the value 10 for all compounds considered; hence the 4d orbitals play no role of importance in the chemical bonding of antimony. Further we see that in all three series SbX_3 , SbX_5 and $\text{Sb}(\text{CH}_3)_3\text{X}_2$ the 5s and 5p populations decrease if we go towards the more electronegative substituent. Comparing our gross 5s populations with the values calculated by Kotheke [13], using the CNDO/2 method, we find somewhat larger values, the difference being in the range 0.08–0.21 for SbX_3 and SbCl_5 and 0.42 for SbF_5 . The qualitative behaviour is the same, however.

In the series $\text{Sb}(\text{CH}_3)_N\text{Cl}_{3-N}$ we observe a fundamentally different behaviour: going towards more electronegative substituents (i.e. towards lower N) we notice a decrease in the $5p_z$ population but an increase in the 5s population. This increase is compatible with the trend in the experimental IS. The decreasing $5p_z$ population corroborates Steven's hypothesis [31], made to rationalize the experimental Mössbauer parameters.

We can use the net orbital populations from table 7 to check the applicability of the Townes–Dailey equation (12). According to this equation one would expect the QS to be proportional to the quantity $\Delta = N_{5p_z} - \frac{1}{2}N_{5p_x} - \frac{1}{2}N_{5p_y}$, which we have listed in the last column. The agreement appears to be poor, there is only a slight correlation between the Δ values and the experimental QS (correlation coefficient 0.67).

Table 8 contains the calculated EFG. The penultimate column contains the quantity $\chi = |(q - q^{\text{el},1})/q|$ which can be considered as a numerical measure for the validity of the assumption that the sum of the two- and three-centre electronic contributions cancels the nuclear contribution. This approximation appears to work quite well.

Table 7
Mulliken gross and net populations of valence orbitals on Sb

Molecule ^{a)}	Gross populations					Net populations					$Z_{\text{Sb}}^{\text{b)}$	$\Delta^{\text{c)}$
	4d	5s	5p _x	5p _y	5p _z	4d	5s	5p _x	5p _y	5p _z		
SbF_3	9.99	1.74	0.47	0.47	0.69	11.26	2.10	0.32	0.32	0.53	1.63	0.21
SbCl_3	9.99	1.85	0.59	0.59	0.88	11.24	2.34	0.38	0.38	0.69	1.10	0.31
SbBr_3	9.98	1.88	0.66	0.66	0.94	11.24	2.37	0.44	0.44	0.77	0.88	0.33
SbI_3 (A)	9.97	1.94	0.74	0.74	0.96	11.22	2.34	0.53	0.53	0.80	0.67	0.27
SbI_3 (B)	9.98	1.94	0.74	0.74	1.05	11.23	2.44	0.51	0.51	0.91	0.58	0.40
SbMeCl_2	9.98	1.79	0.51	0.64	0.95	11.23	2.22	0.32	0.38	0.79	1.13	0.44
SbMe_2Cl	9.98	1.69	0.46	0.60	1.00	11.23	2.09	0.29	0.32	0.87	1.27	0.56
SbMe_3	9.97	1.58	0.54	0.54	1.13	11.22	1.82	0.30	0.30	1.05	1.23	0.75
SbF_5	10.02	1.18	0.50	0.50	0.52	11.29	1.23	0.33	0.33	0.34	2.27	0.01
SbCl_5	10.03	1.41	0.78	0.78	0.80	11.28	1.47	0.51	0.51	0.52	1.21	0.00
SbMe_3F_2	10.01	1.05	0.63	0.63	0.39	11.28	0.93	0.37	0.37	0.27	2.29	-0.10
SbMe_3Cl_2	10.00	1.30	0.67	0.67	0.60	11.26	1.19	0.38	0.38	0.39	1.76	0.00
SbMe_3Br_2	10.00	1.35	0.68	0.68	0.65	11.25	1.27	0.39	0.39	0.46	1.63	0.07
SbMe_3I_2	9.98	1.41	0.67	0.67	0.75	11.24	1.33	0.38	0.38	0.59	1.51	0.21

^{a)} Molecules are placed so that the z axis is the lone-pair axis.

^{b)} Atomic charge of Sb from gross populations.

^{c)} $\Delta = N(5p_z) - \frac{1}{2}N(5p_x) - \frac{1}{2}N(5p_y)$, where the N are net populations; see also text.

Table 8
Field gradients^{a)} (in au) and quadrupole splittings (in mm s⁻¹)

	$q^{el,1}$	$q^{el,2}$	$q^{el,3}$	q^{el}	$\chi^{b)}$	q^{nuc}	$q^{c)}$	$e^2qQ^{d)}$	Average experimental QS
SbF ₃	-3.608	-0.091	0.006	-3.693	0.0069	0.110	-3.58	7.88	19.5
SbCl ₃	-2.726	0.072	0.004	-2.649	0.0125	-0.043	-2.69	5.92	12.8
SbBr ₃	-2.252	0.066	0.004	-2.183	0.0097	-0.048	-2.23	4.91	11.4
SbI ₃ (A)	-1.320	0.030	0.003	-1.288	0.0044	-0.027	-1.31	2.89	5.6
SbI ₃ (B)	-1.921	0.056	0.004	-1.862	0.0043	-0.051	-1.91	4.21	5.6
SbMeCl ₂	-4.407	0.027	-0.011	-4.391	0.0049	-0.037	-4.43	9.74	30.5
SbMe ₂ Cl	-4.576	0.049	0.000	-4.526	0.0025	-0.038	-4.56	10.04	29.2
SbMe ₃	-3.300	0.047	0.013	-3.240	0.0015	-0.065	-3.30	7.27	15.8
SbF ₅	-0.330	-0.034	0.003	-0.362	0.0280	0.040	-0.32	0.71	8.7
SbCl ₅	-0.787	-0.066	0.008	-0.845	0.0088	0.065	-0.78	1.72	-5.1
SbMe ₃ F ₂	2.529	-0.234	0.056	2.351	0.0373	0.276	2.63	-5.78	-
SbMe ₃ Cl ₂	1.518	-0.074	0.052	1.496	0.0399	0.086	1.58	-3.48	-24.0
SbMe ₃ Br ₂	1.026	-0.026	0.049	1.049	0.0518	0.033	1.08	-2.38	-21.7
SbMe ₃ I ₂	1.386	0.012	0.041	1.439	0.0034	-0.048	1.39	-3.06	-19.3

^{a)} Using the frozen-core approximation, no Sternheimer correction applied. ^{b)} $\chi = |(q - q^{el,1})/q|$, see also text.

^{c)} Calculated asymmetry parameters (in parentheses the experimental value): 0.45 (0.35) for SbMeCl₂, 0.93 (0.83) for SbMe₂Cl.

^{d)} Conversion factor: 1 au = 2.2 mm s⁻¹, calculated from $Q = -0.28 \pm 0.06$ barn [66].

In order to calculate the QS we used Steven's value for the nuclear quadrupole moment of ¹²¹Sb, $Q = -0.28 \pm 0.06$ barn [66]. We note, however, that the value of the nuclear quadrupole moment is actually very uncertain[†]. Values ranging from -0.20 to -0.54 barn are found in the literature [39,67,68].

We now compare the calculated QS (with $Q = -0.28$ barn) with experiment. For the series SbX₃ the experimental values are accurately reproduced (correlation coefficient 0.99), apart from a constant factor of 2.3. Further we note that structure A for SbI₃ fits better in the trend than structure B. For the series SbMe_NCl_{3-N} the situation is similar (correlation coefficient 0.98), the factor now is 2.8. Taking the two series together one obtains a factor 2.7 (correlation coefficient 0.97). For SbMe₃X₂ the agreement is much worse (a factor of 7.6, correlation coefficient 0.37) although the discrepancy between Sb(III) and Sb(V) compounds is still not as drastic as in the extended Hückel calculations [6]. The molecules SbF₅ and SbCl₅ show a very irregu-

lar behaviour; one is led to the conclusion that the geometries used are not correct, a conclusion that is supported by the IS calculations (see below), and by Kothekar's QS results [13].

Let us now briefly analyse the possible sources of the discrepancy between the calculated and the experimental QS: the HFS LCAO model, AO basis set deficiency, neglect of relativistic effects, neglect of lattice contributions, neglect of core polarization and finally the uncertainty of the nuclear quadrupole moment. With respect to the method and AO basis used we recall that our calculations on HCl and Guenzburger and Ellis's calculations on linear Au compounds have shown that the HFS LCAO method may yield good QSs with AO bases of similar size as used here. In order to check the influence of the lattice contributions to the EFG we performed a test calculation for SbCl₃, which has an orthorhombic unit cell with lattice parameters $a = 6.37$ Å, $b = 8.12$ Å, $c = 9.47$ Å and as space group Pbnm [57]. We used a point charge model with the Mulliken charges from the HFS LCAO calculation. It took thirty shells of equivalent cells to obtain a result stable to two decimal places. The result is a lattice contribution $q = -4.3 \times 10^{-3}$ au, which means that even with a Sternheimer factor $1 - \gamma_{\infty} \approx 10$ the lattice

[†] This uncertainty arises because the quantity amenable to measurement is the product of Q and the EFG at the nucleus; accurate calculations or independent measurements of the EFG in Sb compounds are not available.

contribution is negligible compared to the contribution of the central SbCl_3 molecule itself.

The Sternheimer corrections for the neglect of core polarization customarily used for Sb are not much greater than unity (1.115 [64], 1.2 [13], 1.23 [6]). The uncertainty in Q may be the key factor: taking $Q = -0.54$ [68] instead of $Q = -0.28$ would yield (together with a Sternheimer factor of 1.4) the factor 2.7 which would lead to very good agreement of the calculated QS with the experimental data for the Sb(III) compounds. At the same time it would reduce the error for the series SbMe_3X_2 to a factor of 3. It is also possible that Q is still larger, however, or that the core polarization effects are more important (actually the 1s–4d Sb core is considerably larger than the 1s–2p core in Cl, where we have calculated a Sternheimer factor of 1.18), while we cannot exclude that relativistic effects might be important, too.

Finally we compare the calculated asymmetry parameters in the two cases where it does not vanish on symmetry grounds: SbMe_2Cl and SbMeCl_2 . As can be seen from table 8 the agreement with experiment is satisfactory.

Fig. 1 shows a plot of the calculated values for the valence-electron density at the Sb nucleus versus the (averaged) experimental isomer shifts (with respect to InSb as source). One observes a very nearly linear behaviour as expected theoretically. The only molecules falling aside are SbF_5

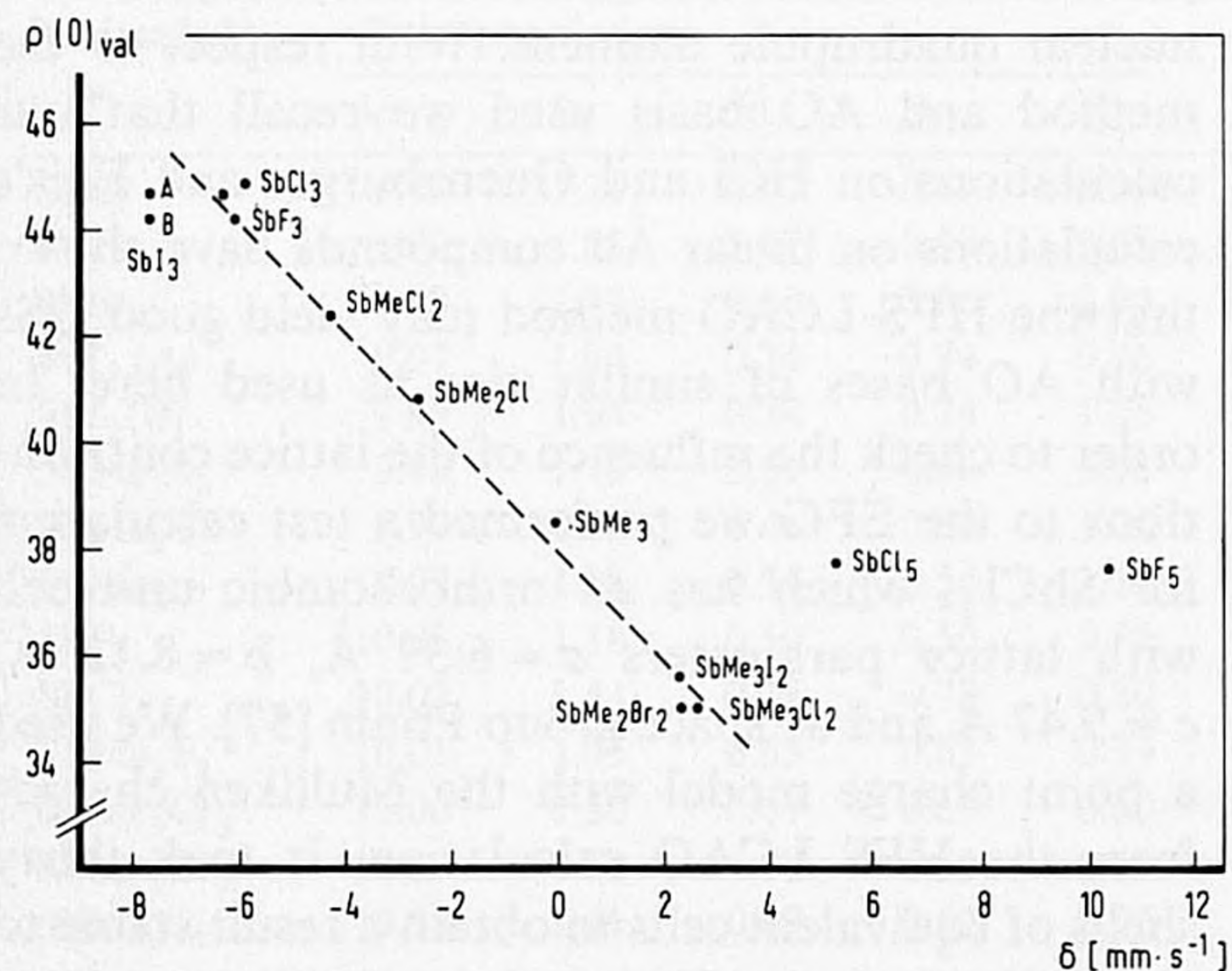


Fig. 1. Relation between the calculated valence-electron density $\rho(0)$ on the Sb nucleus (in 10^{-3} electrons/ a_0^3) and the measured Mössbauer isomer shifts of various Sb compounds.

and SbCl_5 ; the deviation is too large for being explicable in terms of a possible core contribution to $\Delta\rho(0)$. Hence we feel strengthened in our opinion that the trigonal bipyramidal geometry used is not correct for these molecules. Further we note that also the isomer-shift data indicate a preference of structure A over structure B for SbI_3 .

Making a least-squares fit of all points, except SbF_5 , SbCl_5 and $\text{SbI}_3(\text{B})$, and using the value $\frac{4}{3}\pi ZR^2 S'(Z) = 1.303 \times 10^{-24}$ cm s⁻¹ [13], we calculate $\Delta R/R = -1.08 \times 10^{-3}$ (correlation coefficient 0.99), which agrees very well with the values quoted in the literature, ranging from -1.44×10^{-3} to -0.85×10^{-3} [13,34,39,46,65].

Finally we also checked the linear dependency of the experimental IS on the Sb 5s net population, which has been used in semi-empirical calculations (see section 2.1). Again it is possible to obtain a reasonable linear fit of the data; the only two compounds falling aside are SbF_5 and SbCl_5 .

5. Conclusions

In this paper we have investigated the calculation of Mössbauer parameters by means of the Hartree–Fock–Slater LCAO method. Test calculations on HCl have shown that it is possible to obtain results in good agreement with ab initio calculations and experiments. The HFS LCAO all-electron calculations require exceedingly large numbers of numerical integration points, however, which makes the method impractical for larger systems. Frozen-core calculations, on the other hand, yield stable and accurate results (compared with ab initio results) at a standard choice of integration parameters. The price one has to pay is the neglect of core polarization effects, which could be corrected for by use of Sternheimer factors for the quadrupole splitting. Such factors are not accurately known, however, but the frozen-core method can still be useful for looking at relative properties in series of related compounds.

We have applied this method of calculation to a group of thirteen antimony compounds. The calculated quadrupole splittings are consistently too small by a factor of 2.7 (correlation coefficient 0.97) for Sb(III) compounds and a factor of 7.6 for

the Sb(V) compounds $\text{Sb}(\text{CH}_3)_3\text{X}_2$ (correlation coefficient 0.37). These factors may be partly due to core polarization, to the uncertainty in the nuclear quadrupole moment, and, possibly, relativistic effects. The qualitative features of the experimental data are very well reproduced, however, especially for the Sb(III) compounds. It is striking that also the extended Hückel and CNDO/2 results for Sb(V) compounds show the same type of discrepancy (with a factor that is even larger).

For the isomer shift the agreement between the calculated and experimental data is very good, not only qualitatively, but also quantitatively. A linear relation between the valence-electron density at the Sb nucleus and the experimental isomer shift is satisfied for all compounds except SbF_5 and SbCl_5 . From this relation we derive a value $\Delta R/R = -1.08 \times 10^{-3}$ for the Sb nucleus, in agreement with other values given in the literature.

Our results support Stevens' hypothesis that in the series $\text{Sb}(\text{CH}_3)_N\text{Cl}_{3-N}$ the 5s character of the bonding increases, while the 5p character decreases for decreasing N . In the series SbX_3 and SbX_5 we find decreasing 5s and 5p character with the more electronegative X.

Finally, we note that the comparison of our QS and IS results with the experimental data leads to some suggestions about the structures of some of the molecules. We think that the trigonal bipyramidal structures for SbF_5 and SbCl_5 which have been proposed (but not yet confirmed by X-ray diffraction) need reconsideration. Among the two structures proposed for SbI_3 , we prefer the structure (A) with the larger I-Sb-I angle.

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References

- [1] J.A. Tossel, *J. Chem. Phys.* 66 (1977) 5712;
A. Tang Kai, H. Annersten and T. Ericsson, *Phys. Chem. Miner.* 5 (1980) 343;
M. Braga, A.C. Pavao and J.R. Leite, *Phys. Rev. B* 23 (1981) 4328;
M. Braga and C.A. Taft, *J. Chem. Phys.* 74 (1981) 2969.
- [2] W.C. Nieuwpoort, D. Post and P.T. van Duynen, *Phys. Rev. B* 17 (1978) 91, and references therein;
P.S. Bagus, U.I. Walgren and J. Almlöf, *J. Chem. Phys.* 64 (1976) 2324.
- [3] E.J. Baerends, D.E. Ellis and P. Ros, *Chem. Phys.* 2 (1973) 41;
E.J. Baerends and P. Ros, *Chem. Phys.* 2 (1973) 52.
- [4] P.J.M. Geurts, J.W. Gosselink, A. van der Avoird, E.J. Baerends and J.G. Snijders, *Chem. Phys.* 46 (1980) 133.
- [5] D. Guenzburger and D.E. Ellis, *Phys. Rev. B* 22 (1980) 4203.
- [6] J.G. Stevens and C.P. Keijzers, private communication.
- [7] J.C. Slater, *Advan. Quantum Chem.* 6 (1972) 1; *Quantum theory of molecules and solids*, Vol. 4 (McGraw-Hill, New York, 1974).
- [8] D.E. Ellis, *Intern. J. Quantum Chem.* 2S (1968) 35;
D.E. Ellis and G.S. Painter, *Phys. Rev. B* 2 (1970) 2887.
- [9] K.H. Johnson, *J. Chem. Phys.* 45 (1966) 3085;
K.H. Johnson and F.C. Smith Jr., *Phys. Rev. B* 5 (1972) 831;
J.C. Slater and K.H. Johnson, *Phys. Rev. B* 5 (1972) 844.
- [10] E.J. Baerends and P. Ros, *Chem. Phys.* 8 (1975) 412;
Intern. J. Quantum Chem. 12S (1978) 169.
- [11] T.C. Gibb, *Principles of Mössbauer spectroscopy* (Chapman and Hall, London, 1975);
G.M. Kalvius, *Hyperfine interaction in excited nuclei* (Academic Press, New York, 1972) p. 523.
- [12] D.A. Shirley, *Rev. Mod. Phys.* 36 (1964) 339.
- [13] V. Kothekar, *Intern. J. Quantum Chem.* 10 (1976) 993, and references therein.
- [14] E.A.C. Lucken, *Nuclear quadrupole coupling constants* (Academic Press, New York, 1969).
- [15] C.H. Townes and B.P. Dailey, *J. Chem. Phys.* 17 (1949) 782.
- [16] J.V. Mallow, A.J. Freeman and J.P. Desclaux, *Phys. Rev. B* 13 (1976) 1884.
- [17] R.M. Sternheimer, *Phys. Rev.* 164 (1967) 10, and references therein.
- [18] S.L. Ruby, G.M. Kalvius, G.B. Beard and R.E. Snijder, *Phys. Rev.* 159 (1967) 239;
T.P. Das and R. Bersohn, *Phys. Rev.* 131 (1963) 250;
K.D. Sen and P.C. Schmidt, *Phys. Rev. A* 23 (1981) 1026;
P.C. Schmidt, K.D. Sen, T.P. Das and A. Weiss, *Phys. Rev. A* 22 (1980) 4167;
K.D. Sen and P.T. Narasimhan, *Phys. Rev. B* 16 (1977) 107.
- [19] E.J. Baerends, and P. Ros, HFS LCAO program, Scheikundig Laboratorium der Vrije Universiteit, Amsterdam, The Netherlands.

- [20] D.B. Neumann, H. Basch, R.L. Kornegay, L.C. Snijder, J.W. Moscowitz, C. Hornback and S.P. Liebman, *QCPE* 11 (1971) 199.
- [21] R.F. Stewart, *J. Chem. Phys.* 52 (1970) 431.
- [22] A.D. McLean and M. Yoshimine, *J. Chem. Phys.* 47 (1967) 3256.
- [23] P.E. Cade and W.M. Huo, *J. Chem. Phys.* 47 (1967) 649.
- [24] D.E. Ellis, private communication.
- [25] J.D. Petke and J.L. Whitten, *J. Chem. Phys.* 56 (1972) 830.
- [26] E. Scrocco and J. Tomasi, *Theoret. Chim. Acta* 2 (1964) 386.
- [27] J.E. Grabenstetter and M.A. Whitehead, *Mol. Phys.* 34 (1977) 1577.
- [28] R. Moccia, *Theoret. Chim. Acta* 8 (1967) 8.
- [29] P. Vernooijs, J.G. Snijders and E.J. Baerends, Slater type basis functions for the whole periodic system, Internal Report, Free University, Amsterdam, The Netherlands (1981).
- [30] L.H. Bowen and G.G. Long, *Inorg. Chem.* 15 (1976) 1039, and references therein.
- [31] J.G. Stevens, J.M. Trooster, M.A. Meinema and J.G. Nottes, *Inorg. Chem.* 20 (1981) 801.
- [32] G.D. Fong, R.R. Kuckowski and A.J. Ashe, *J. Mol. Spectry.* 70 (1978) 197, and references therein.
- [33] R.G. Hyde and J. B. Peel, *Mol. Phys.* 33 (1979) 887.
- [34] D.I. Baltranas, S.P. Ionov, A.Yu. Alexandrov and E.F. Makarov, *Chem. Phys. Letters* 20 (1973) 55.
- [35] J.P. Devort and J.M. Friedt, *Chem. Phys. Letters* 35 (1975) 423.
- [36] J.D. Donaldson, J.T. Southern and M.J. Tricker, *J. Chem. Soc. Dalton Trans.* (1972) 893.
- [37] L.H. Bowen, J.G. Stevens and G.G. Long, *J. Chem. Phys.* 51 (1969) 2010.
- [38] V.P. Gor'kov, R.L. Davidovich, G.V. Zimina, L.A. Sadokhina, F.Kh. Chibirova and V.S. Shpinel, *Koord. Khim.* 1 (1975) 561.
- [39] S.L. Ruby, G.M. Kalvius, G.B. Beard and R.E. Snijder, *Phys. Rev.* 159 (1967) 239.
- [40] J.G. Stevens and L.H. Bowen, in: *Mössbauer effect methodology*, Vol. 5, ed. I.J. Graverman (Plenum Press, New York, 1970) p. 27.
- [41] J.G. Ballard, T. Birchall, R. Fourcade and G. Mascherpa, *J. Chem. Soc. Dalton Trans.* (1976) 2409.
- [42] J.P. Devort, J.P. Sanchez, J.M. Friedt and G.K. Shenoy, *J. Phys. (Paris) C-6* 35 (1974) 255.
- [43] J.G. Stevens and J.M. Trooster, *J. Chem. Soc. Dalton Trans.* (1979) 740.
- [44] F. Petillon and J.E. Guerschais, *J. Inorg. Nucl. Chem.* 37 (1975) 1863.
- [45] L.H. Bowen, K.A. Taylor, H.K. Chin and G.G. Long, *J. Inorg. Nucl. Chem.* 36 (1974) 101.
- [46] V. Kothekar, B.Z. Iofa, S.I. Semonov and V.S. Shpinel, *Soviet Phys. JETP* 28 (1969) 86.
- [47] A.Yu. Alexandrov, D.I. Baltranas, L.M. Belyaev, I.S. Lyubutin and V.A. Lyakhovitskaya, *Kristallografiya* 17 (1972) 332.
- [48] T.B. Brill, G.E. Parris, G.G. Long and L.H. Bowen, *Inorg. Chem.* 12 (1973) 1888.
- [49] J.G. Stevens and S.L. Ruby, *Phys. Letters* 32A (1970) 91.
- [50] G.G. Long, J.G. Stevens, R.J. Tullbane and L.H. Bowen, *J. Am. Chem. Soc.* 92 (1970) 4230.
- [51] K. Dehnicke, K. Fleck, K. Schmidt and J. Pebler, *Z. Anorg. Allg. Chem.* 451 (1979) 109.
- [52] G.K. Shenoy and J.M. Friedt, *Phys. Rev. Letters* 31 (1973) 419.
- [53] J.G. Ballard and T. Birchall, *J. Chem. Soc. Dalton Trans.* (1976) 1859.
- [54] T. Birchall and J.G. Ballard, *J. Phys. (Paris) C-6* 37 (1976) 513.
- [55] Sh.Sh. Bashkirov and G.Ya. Selyatin, *Soviet Phys. Solid State* 9 (1968) 2284.
- [56] V.S. Shpinel, V.A. Bryukhanov, V. Kothekar, B.Z. Iofa and S. Semonov, *Symp. Faraday Soc.* 1 (1968) 69.
- [57] I. Lindquist and A. Niggli, *J. Inorg. Nucl. Chem.* 2 (1956) 345.
- [58] D.W. Cushen and R. Hulme, *J. Chem. Soc.* (1962) 2218.
- [59] A.F. Wells, *Structural inorganic chemistry* (Clarendon Press, Oxford, 1962) pp. 663, 693.
- [60] T.N. Polynova and M.A. Poraj-Koshic, *Zh. Strukt. Khim.* 7 (1966) 642.
- [61] W. Schwartz and H.J. Guder, *Z. Anorg. Allg. Chem.* 444 (1978) 105.
- [62] A.F. Wells, *Z. Krist.* 99 (1938) 367.
- [63] W. Schwartz and H.J. Guder, *Z. Naturforsch.* 33b (1978) 485.
- [64] E.H. Huygh and T.P. Das, *Phys. Rev.* 143 (1966) 452.
- [65] V.A. Brakhanov, B.Z. Iofa, V. Kothekar, S.I. Simonov and V.S. Shpinel, *Soviet Phys. JETP* 26 (1968) 912.
- [66] J.G. Stevens and V.E. Stevens, *Mössbauer effect data index 1976* (IFI/Plenum, New York, 1976).
- [67] C.M. Lederer and V.S. Shirley, eds., *Tables of isotopes*, 7th Ed. (Wiley, New York, 1978).
- [68] K. Murakawa and S. Suwa, *Phys. Rev.* 76 (1949) 433.