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## Isomer shifts and chemical bonding in crystalline Sn(II) and Sn(IV) compounds

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**Abstract.** First-principles self-consistent local-density calculations of the electronic structure of clusters representing Sn(II) (SnO, SnF<sub>2</sub>, SnS and SnSe) and Sn(IV) (SnO<sub>2</sub> and SnF<sub>4</sub>) crystalline compounds were performed. Values of the electron density at the Sn nucleus were obtained and related to measured values of the Mössbauer isomer shifts reported in the literature. The nuclear parameter of <sup>119</sup>Sn derived was  $\Delta R/R = (1.58 \pm 0.14) \times 10^{-4}$ . The chemical bonding in the solids was analysed and related to the electron densities obtained.

### 1. Introduction

Hyperfine interactions, as measured by Mössbauer spectroscopy, may give valuable information on the chemical environment around a Mössbauer atom. However, as such interactions are described by a product of a nuclear term and an electronic term, the qualitative and quantitative interpretation of the measurements depend on a reliable estimate of the nuclear term.

The isomer shift  $\delta$  is the product of a nuclear term of the Mössbauer isotope, which is the relative variation  $\Delta R/R$  of the nuclear radius in the Mössbauer transition, and an electronic term, the difference between the electron densities at the nucleus of the absorber and source [1]. Reliable calculations of the electronic term, when coupled with the measured values of  $\delta$ , may thus lead to a determination of  $\Delta R/R$ . Knowledge of  $\Delta R/R$ , with a reasonable degree of precision, is essential for the experimentalists to interpret the measured data.

In the case of the Mössbauer isotope <sup>119</sup>Sn, reported electronic structure calculations for the investigation of hyperfine parameters have been noticeably fewer than for the better-studied isotope <sup>57</sup>Fe. In the days of greater development of Mössbauer spectroscopy (the 1960s), Fe was investigated theoretically with the aid of the crystal-field and ligand-field theories for transition-metal compounds; however, no such models were available for Sn. The current, much more powerful methods have been applied only scarcely to Sn metal, compounds and alloys; one reason for this is probably the very complex crystal structures displayed by some of the solids.

On the experimental side, a large number of data on isomer shifts of Sn metal, alloys and compounds is available in the literature [1, 2]. It is thus desirable to perform

electronic structure calculations both to derive a reasonably accurate value for the nuclear term and to correlate the  $\delta$ -values to the characteristics of the chemical bonds.

We report first-principles electronic structure calculations for clusters representing the solid compounds SnO (black), SnF<sub>2</sub>( $\beta$ ), SnS, SnSe, SnO<sub>2</sub> and SnF<sub>4</sub>. The values of the electron densities at the nucleus were obtained and correlated to measured  $\delta$ -values reported in the literature. The choice of these compounds was made on the basis of the following considerations: they cover a wide range of  $\delta$ -values; they include both Sn(II) and Sn(IV) compounds; the anions cover a wide range of electronegativities and are thus expected to bond to Sn in different ways; the solids have well defined crystal structures; last but not least, they include compounds with practical and technological importance [3]. In fact, SnO<sub>2</sub> is a large-gap semiconductor, and its stability in the laboratory has made it widely used as a source in Mössbauer spectroscopy. It has important optical properties, acting as a transparent electrode and as material for optical covering. SnS and SnSe are group IV–VI semiconductors with a layered structure.

The first-principles method employed is the self-consistent discrete variational method (DVM) [4] in the framework of the local-density (LD) theory [5]. Calculations were performed for several clusters of different sizes, for each compound, to test the effect of cluster size. In all clusters, the Sn atom where the electron density was calculated was placed at the centre, as this site has no truncated bonds and thus simulates in a better way a Sn atom in the solid. An embedding scheme was adopted to take into account the external infinite crystal. The electronic structures were obtained, as well as the electron densities at the nucleus of the central Sn atom, which were related to  $\delta$ -values to derive a value of  $\Delta R/R$ .

The organization of this paper is as follows: in section 2 we describe the theoretical method, in section 3 we present and discuss our results pertaining to the isomer shifts, correlating them to the chemical bonding in the solids and in section 4 we give a brief summary of our main conclusions.

## 2. Theoretical method

The purpose of the DVM [4] is to solve the set of one-electron Kohn–Sham [6] equations of LD theory for the cluster (in hartrees):

$$h\psi_i(\mathbf{r}) = [-\frac{1}{2}\nabla^2 + V_C(\mathbf{r}) + V_{xc}(\mathbf{r})]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}). \quad (1)$$

In equation (1), the Coulomb potential  $V_C(\mathbf{r})$  includes the electron–nucleus attraction and electron–electron repulsion, and  $V_{xc}(\mathbf{r})$  is the exchange–correlation potential, which we have chosen in the form derived by Hedin and Lundqvist [7].  $V_{xc}(\mathbf{r})$  is a functional of the electron density calculated with the cluster orbitals  $\psi_i(\mathbf{r})$ , with occupation  $n_i$ :

$$\rho(\mathbf{r}) = \sum_i n_i |\psi_i(\mathbf{r})|^2. \quad (2)$$

The cluster orbitals are expanded [8] on a basis of numerical symmetrized atomic orbitals  $\chi_\mu^s$ :

$$\psi_i(\mathbf{r}) = \sum_\mu \chi_\mu^s(\mathbf{r}) C_\mu^i. \quad (3)$$

The discrete variational scheme leads to the secular equations

$$([H] - [E][S])[C] = 0 \quad (4)$$

where the matrix elements of the Hamiltonian matrix  $[H]$  and overlap matrix  $[S]$  are summations over a three-dimensional grid of points  $r_j$ :

$$\sum_j w(r_j) \chi_\mu^{s*}(r_j) h(r_j) \chi_\nu^s(r_j) \quad \text{and} \quad \sum_j w(r_j) \chi_\mu^{s*}(r_j) \chi_\nu^s(r_j) \quad (5)$$

and  $w(r_j)$  is the weight per point. The three-dimensional grid is regular inside a sphere, around the central Sn atom, of radius equal to  $2a_0$ , where a precise polynomial integration is performed [9]; outside this sphere, and around all other atoms, the pseudo-random Diophantine point generator provides the points. The total number of points employed here were in the range 15 000–19 000.

To facilitate the computation of the electron–electron repulsion term, a model charge density  $\rho_M(\mathbf{r})$  is used in place of the exact cluster charge density [10]:

$$\rho(\mathbf{r}) \approx \rho_M(\mathbf{r}) = \sum_{nl} d_{nl}^l \rho_{nl}^l(\mathbf{r}) \quad (6)$$

where  $\rho_{nl}^l(\mathbf{r})$  are overlapping charge densities centred at each atom  $q$ , calculated with the radial atomic functions of the basis

$$\rho_{nl}^l(\mathbf{r}) = \sum_q |R_{nl}^q(r_q)|^2 Y_0^l(\hat{r}_q). \quad (7)$$

The summation is over a previously defined set of atoms and  $l$  represents a particular set. In the present calculations, the central Sn atom ( $\text{Sn}_c$ ), which is better represented in all clusters and where  $\delta$  will be calculated, is kept as a set by itself. All peripheral Sn atoms ( $\text{Sn}_p$ ) constitute another set. As for the anions, they will be kept in the same set if all anions are equivalent in the crystal ( $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{SnS}$  and  $\text{SnSe}$ ); otherwise, there will be a different set for each type of anion ( $\text{SnF}_2$  and  $\text{SnF}_4$ ). The coefficients  $d_{nl}^l$  are obtained variationally by a least-squares procedure [10], with the condition that  $\rho_M(\mathbf{r})$  integrates to the total number of electrons in the cluster. Self-consistency is achieved through convergence of these coefficients, since they ultimately define the cluster potential.

In the calculations reported here, the atomic basis functions were obtained from numerical self-consistent atomic LD calculations. Basis functions in the variational space were 4s, 4p, 4d, 5s and 5p for  $\text{Sn}_c$ , 5s and 5p for  $\text{Sn}_p$ , 3s and 3p for S, and 4s and 4p for Se. For O and F all orbitals were included.

Core orbitals not kept in the variational space were orthogonalized to the valence basis functions in the first iteration and kept 'frozen' subsequently.

An embedding scheme was adopted to take into account the effect of the atoms external to the cluster in the solid. At each site of several layers of atoms is placed a numerical atomic charge density, truncated at the core region to simulate the Pauli exclusion principle [11]. More distant charges were taken into account by a Ewald procedure [12].

Cluster calculations for these ionic and partially ionic solids pose a number of questions derived from the truncation of bonds to form the cluster. One of these questions is the definition of the charge on the cluster. We have approached this problem by employing a scheme by which the charge on the cluster is not defined beforehand but

is consistent with the atomic charges found in the calculations. The scheme is as follows: to start the self-consistent procedure, the atoms are considered neutral. Accordingly, basis functions are generated for neutral atoms; neutral atoms also are placed in the external shells of the embedding, and the cluster charge is zero. After self-consistency is achieved, a Mulliken [13] population analysis is performed and charges are obtained for the atoms. New basis functions are generated for the atoms with the charges and configurations obtained, as well as new charge densities for the embedding. For Sn, the central atom is considered, since it is better described. A new charge for the cluster is defined; for example, if the charge found for  $\text{Sn}_c$  is +1 in  $[\text{SnO}_8\text{Sn}_{12}]$  representing SnO, the oxygen atoms are assumed to have charge -1 and the charge of the cluster is thus +5. This charge defines the total number of electrons for the next set of iterations. This computer-time-consuming procedure is repeated until the charges and configurations of the cluster atoms, the atoms generating the basis functions and the atoms of the embedding are similar. With this procedure we reduce spurious effects of basis truncation and of finite cluster size, since basis functions and external atoms are consistent with the results for the cluster.

The isomer shift  $\delta$  is defined as [1, 2]

$$\delta = \frac{4}{3}\pi Ze^2 S'(Z) R^2 (\Delta R/R) [\rho_a(0) - \rho_s(0)] \quad (8)$$

where  $R$  is the radius of a spherical nucleus,  $Z$  is the atomic number,  $S'(Z)$  a correction for relativistic effects and the term in square brackets is the difference between the electron densities (equation (2)) at the nucleus of the absorber and the source. Alternatively,  $\delta$  may be expressed as

$$\delta = \frac{2}{3}\pi e^2 Z S'(Z) \Delta \langle r^2 \rangle [\rho_a(0) - \rho_s(0)] \quad (9)$$

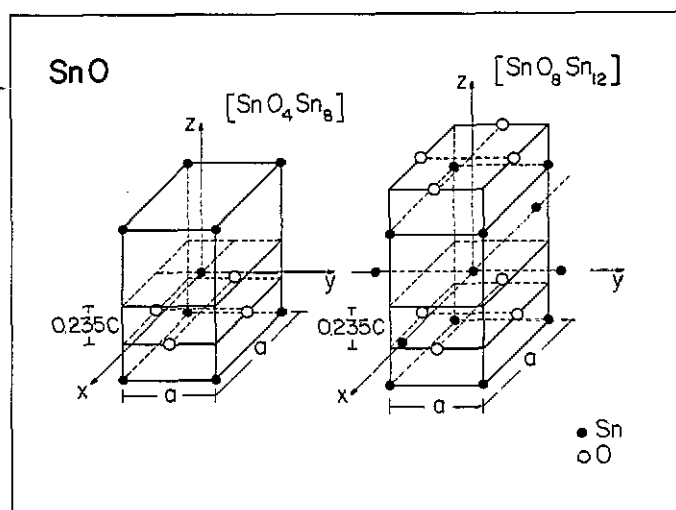
where  $\Delta \langle r^2 \rangle$  is the change in the mean square radius of the nucleus in the Mössbauer transition. The value of  $S'(Z)$  for  $^{119}\text{Sn}$  (2.306) was taken from Shirley's [14] early derivation; more accurate relativistic and non-relativistic LD atomic calculations have demonstrated that this linear correction is quite adequate [15].

### 3. Isomer shifts and chemical bonding

In table 1 is given structural information on the solid compounds and on the clusters chosen to represent them [16–21]. The crystal structures are complex, resulting in very low point symmetries around the central Sn atom for the clusters, in most cases. In figures 1–5 are depicted clusters chosen to represent the crystals. Convergence of the value of  $\rho(0)$  with cluster size was tested for all compounds, and it was verified to be adequate; accordingly, the largest cluster considered for each compound was chosen to represent the solid. This study of the influence of cluster size on a given property, however time consuming, has made it clear that caution is needed with cluster calculations of isomer shifts. For example, the addition of the four topmost oxygen atoms (see figure 1) to the smallest cluster representing SnO ( $[\text{SnO}_4\text{Sn}_8]$ ) changes the value of  $\rho(0)$  significantly; further inclusion of the four peripheral Sn atoms to form  $[\text{SnO}_8\text{Sn}_{12}]$ , however, has a small effect on  $\rho(0)$ . The value of  $\rho(0)$  for  $[\text{SnS}_7\text{Sn}_2]$  representing SnS is very different from that obtained for  $[\text{SnS}_7\text{Sn}_6]$ ;  $\rho(0)$  for this last cluster, however, does not differ much from that obtained for  $[\text{SnS}_7\text{Sn}_8]$ . Accordingly, SnS and SnSe, which have the same crystal structure, were represented by  $[\text{SnS}_7\text{Sn}_8]$  and  $[\text{SnSe}_7\text{Sn}_8]$ , respectively. The two Sn(IV) compounds  $\text{SnO}_2$  and  $\text{SnF}_4$  have sixfold-coordinated nearest

**Table 1.** Information on the crystal structures of Sn(II) and Sn(IV) solids, clusters for which calculations were performed and point symmetry around central Sn atoms.

Compound	Crystal structure [16]	Lattice parameters (Å)	Sn-X nearest-neighbour distances (Å)	Clusters	Local symmetry
SnO (black) [17]	Tetragonal	$a = 3.80$ $c = 4.84$	4(O)2.22	[SnO <sub>4</sub> Sn <sub>8</sub> ] [SnO <sub>8</sub> Sn <sub>8</sub> ] [SnO <sub>8</sub> Sn <sub>12</sub> ]	C <sub>4v</sub>
SnF <sub>2</sub> (β) [18]	Orthorhombic	$a = 4.98$ $b = 5.14$ $c = 8.48$	1(F)1.89 1(F)2.26 1(F)2.40 1(F)2.41 1(F)2.49	[SnF <sub>5</sub> ] [SnF <sub>11</sub> Sn <sub>4</sub> ]	C <sub>1</sub>
SnS [19]	Orthorhombic	$a = 4.33$ $b = 11.18$ $c = 3.98$	1(S)2.62 2(S)2.68 2(S)3.27 1(S)3.39	[SnS <sub>7</sub> Sn <sub>2</sub> ] [SnS <sub>7</sub> Sn <sub>6</sub> ] [SnS <sub>7</sub> Sn <sub>8</sub> ]	C <sub>s</sub>
SnSe [19]	Orthorhombic	$a = 4.46$ $b = 11.57$ $c = 4.19$	1(Se)2.77 2(Se)2.82 2(Se)3.35 1(Se)3.47	[SnSe <sub>7</sub> Sn <sub>8</sub> ]	C <sub>s</sub>
SnO <sub>2</sub> [19, 20]	Tetragonal	$a = 4.74$ $c = 3.19$	2(O) <sub>y</sub> 2.06 4(O) <sub>xz</sub> 2.05	[SnO <sub>6</sub> ] [SnO <sub>6</sub> Sn <sub>2</sub> ] [SnO <sub>10</sub> Sn <sub>10</sub> ]	D <sub>2h</sub>
SnF <sub>4</sub> [21]	Tetragonal	$a = 4.04$ $c = 7.93$	4(F) <sub>xy</sub> 2.02 2(F) <sub>z</sub> 1.88	[SnF <sub>6</sub> ] [SnF <sub>14</sub> Sn <sub>4</sub> ] [SnF <sub>22</sub> Sn <sub>4</sub> ]	D <sub>4h</sub>

**Figure 1.** The smallest and the largest clusters selected to represent SnO (black).

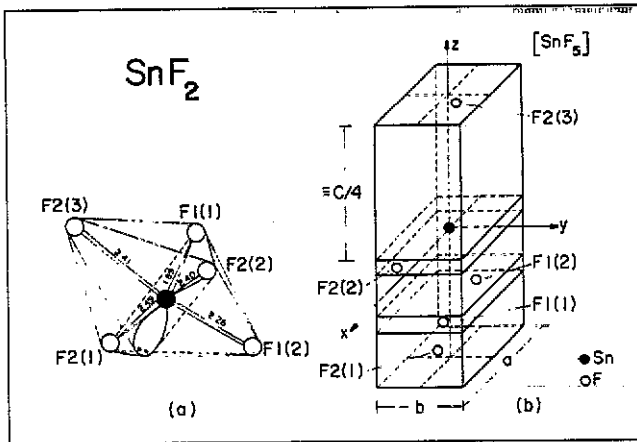


Figure 2. (a) Closest F neighbour environment surrounding a Sn atom in  $\text{SnF}_2$ . The small full circles represent 'lone-pair' electrons. F1 and F2 are the two types of F atoms in the  $\text{SnF}_2$  crystal. Sn nearest-neighbour distances are also given (in ångströms). (b) Smallest cluster selected to represent  $\text{SnF}_2$ . The largest cluster is not depicted because of the complexity of the low-symmetry structure.

neighbours; however, it was verified that inclusion of more distant Sn and anion atoms to the minimal clusters  $[\text{SnO}_6]$  and  $[\text{SnF}_6]$  (see table 1) is essential to obtain accurate values of  $\rho(0)$ .

In table 2 are given the values found for the electron densities  $\rho(0)$  at the nucleus of the neutral Sn atom for the largest clusters representing the Sn(II) and Sn(IV) compounds. The contribution due to the deep core orbitals of Sn was not included, since these orbitals were 'frozen'. In the table, the total  $\rho(0)$  is divided in the contribution due

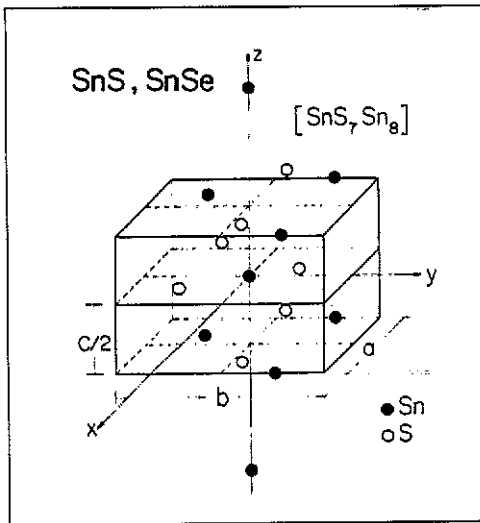


Figure 3. Largest cluster considered to represent isomorphous SnS and SnSe.

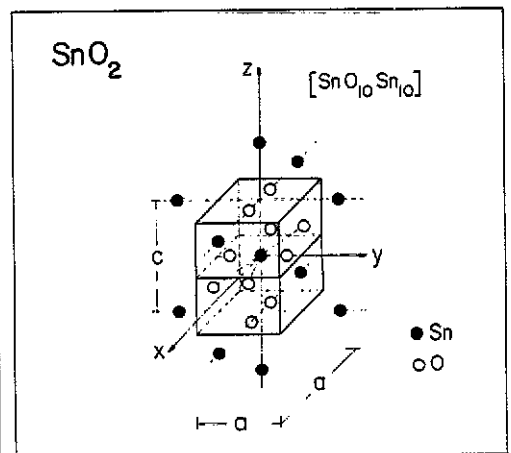


Figure 4. Largest cluster selected to represent  $\text{SnO}_2$ .

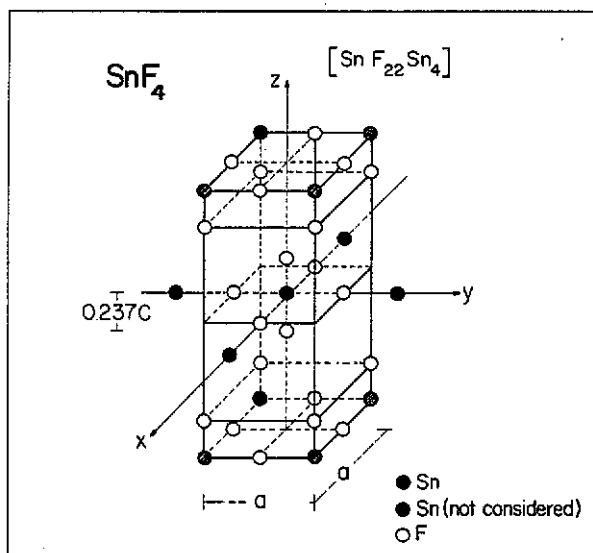


Figure 5. Largest cluster selected to represent SnF<sub>4</sub>.

to the 'shallow core' (cluster orbitals dominated by Sn 4s, 4p and 4d orbitals) and valence contribution, dominated by Sn 5s; this separation, however, was done primarily as an aid to the understanding of the origin of the isomer shifts, since a small mixture of 'shallow core' and valence orbitals is always present. It is seen from the table that differences between the 'shallow core' contributions are much smaller than differences between valence  $\rho(0)$ ; however, they are by no means negligible. This shows the importance of including these inner orbitals in the calculations of  $\delta$ ; their small participation in bonding generates non-negligible differences in  $\rho(0)$ , due to the enhancement brought in by the much greater  $\rho(0)$  of Sn 4s, relative to Sn 5s. Deeper core orbitals may be expected to have approximately equal values of  $\rho(0)$  in all compounds, thus contributing negligibly to isomer shifts.

Regarding the valence  $\rho(0)$ , it may be verified that, as expected, the Sn(IV) compounds SnO<sub>2</sub> and SnF<sub>4</sub> present a much smaller value, relative to Sn(II) compounds; this is in accord with the much lower values of  $\delta$ , since the nuclear term in equation (8) (or equation (9)) is expected to be positive for <sup>119</sup>Sn. As for the Sn(II) compounds, values of  $\rho(0)$  are close together for SnF<sub>2</sub>, SnS and SnSe; accordingly,  $\delta$ -values are similar. SnO has a lower  $\delta$  and, for this compound, a smaller  $\rho(0)$  was obtained with the calculations.

In table 2 are also given the charges and 5s and 5p populations at the central Sn atom, obtained by a Mulliken [13] population analysis of the cluster orbitals. It may be observed that charges for Sn(II) and Sn(IV) compounds are very far from the formal +2 and +4. There is a high degree of 5s-5p hybridization in all compounds. Values of  $\rho(0)$  are inversely proportional to the charge on Sn<sub>c</sub>, for the Sn(II) compounds, with the exception of SnF<sub>2</sub>. In fact, SnO, SnS and SnSe present a large degree of covalency, evidenced by charges on Sn much smaller than +2 and by a high degree of 5s-5p hybridization; on the other hand, SnF<sub>2</sub> has a much larger positive charge and smaller s-p hybridization, with a configuration which resembles more the ionic Sn<sup>2+</sup> 5s<sup>2</sup>5p<sup>0</sup>.



**Table 2.** Electron densities  $\rho(0)$  at the nucleus of the central Sn atom for the largest clusters representing Sn(II) and Sn(IV) compounds. The shallow core is 4s-, 4p- and 4d-containing cluster orbitals. Also given in the table are charges and Mulliken populations on central Sn atom. The  $\delta$ -values are relative to those for SnO<sub>2</sub>.

Compound	Cluster	$\rho(0)$ (units of $a_0^{-3}$ )	Charge on Sn <sub>c</sub>	Populations on Sn <sub>c</sub>	$\delta$ [2] (mm s <sup>-1</sup> )	
SnO	[SnO <sub>8</sub> Sn <sub>12</sub> ]	Shallow core	314.90	+1.25	5s 1.37	2.71
		Valence	27.40		5p 1.39	
		Total	342.30			
SnF <sub>2</sub>	[SnF <sub>11</sub> Sn <sub>4</sub> ]	Shallow core	314.73	+1.68	5s 1.66	3.20
		Valence	35.04		5p 0.67	
		Total	349.77			
SnS	[SnS <sub>7</sub> Sn <sub>8</sub> ]	Shallow core	315.64	+1.03	5s 1.61	3.16
		Valence	31.29		5p 1.36	
		Total	346.93			
SnSe	[SnSe <sub>7</sub> Sn <sub>8</sub> ]	Shallow core	315.51	+0.86	5s 1.71	3.30
		Valence	32.17		5p 1.43	
		Total	347.68			
SnO <sub>2</sub>	[SnO <sub>10</sub> Sn <sub>10</sub> ]	Shallow core	315.76	+2.82	5s 0.49	0
		Valence	13.71		5p 0.70	
		Total	329.47			
SnF <sub>4</sub>	[SnF <sub>22</sub> Sn <sub>4</sub> ]	Shallow core	315.81	+2.80	5s 0.57	-0.47
		Valence	15.29		5p 0.64	
		Total	331.10			

Qualitative analysis of isomer shifts of Sn(II) compounds have stressed the importance of the role played by the 'lone-pair' electrons of Sn<sup>2+</sup>. In fact, in figures 1–3 it may be seen that in Sn(II) compounds the crystals allow a portion of three-dimensional space around a Sn atom to accommodate the 'lone pair'. In a molecular orbital (or cluster orbital) picture like the present one, the 'lone pair' is described by one or more molecular orbitals (or cluster orbitals) presenting a high degree of hybrid 5s and 5p character, since the 'lone-pair' electrons are accommodated in a directional orbital. For SnO (see figure 1) the 'lone pair' is on the z axis, and for SnS and SnSe (see figure 3) in the x–y plane.

The Mulliken population analysis of the Sn(II) compounds shows that the 5s charge is distributed among a large number of valence cluster orbitals in SnO, SnS and SnSe, in accordance with their covalent nature; for SnF<sub>2</sub>, which is much more ionic, this feature is much less pronounced. In all cases, one may indicate one or two orbitals with considerable 5s–5p populations at Sn<sub>c</sub>, which may be identified as 'lone-pair' orbitals of the central Sn atom. These are given in table 3; two orbitals (13a<sub>1</sub> and 15a<sub>1</sub>) may be classified in this manner for SnO, and one (28a') for SnS and SnSe. These orbitals have similar 5s and 5p character on Sn<sub>c</sub>. In contrast, the 5s–5p hybrid orbital of SnF<sub>2</sub> (58a) has a much higher 5s-to-5p ratio, in accordance with the more ionic configuration similar to 5s<sup>2</sup>5p<sup>0</sup>, for Sn<sub>c</sub> (see table 2).

Table 3. Energy and charge distribution of the 'lone-pair' cluster orbitals of the largest clusters representing Sn(II) compounds, as well as their contribution to the electron densities  $\rho(0)$  at the nucleus of the central Sn atom.

Compound	Cluster	Orbital	Energy (eV)	Population analysis (%)			Contribution to $\rho(0)$ (units of $a_0^{-3}$ )	Total valence $\rho(0)$ (units of $a_0^{-3}$ )
				Sn, 5s	Sn, 5p	Sn, p		
SnO	[SnO <sub>8</sub> Sn <sub>12</sub> ]	13a <sub>1</sub>	-12.22	8.6	8.5(5p <sub>z</sub> )	54.8	3.59	27.40
		15a <sub>1</sub>	-10.49	13.6	20.1(5p <sub>z</sub> )	36.3	5.54	
SnF <sub>2</sub>	[SnF <sub>11</sub> Sn <sub>4</sub> ]	58a	-6.38	49.9	12.9	11.7	20.30	35.04
SnS	[SnS <sub>7</sub> Sn <sub>8</sub> ]	28a'	-9.35	12.8	14.9(5p <sub>x</sub> , 5p <sub>y</sub> )	18.5	6.46	31.29
SnSe	[SnSe <sub>7</sub> Sn <sub>8</sub> ]	28a'	-8.19	14.2	14.3(5p <sub>x</sub> , 5p <sub>y</sub> )	15.9	7.24	32.17

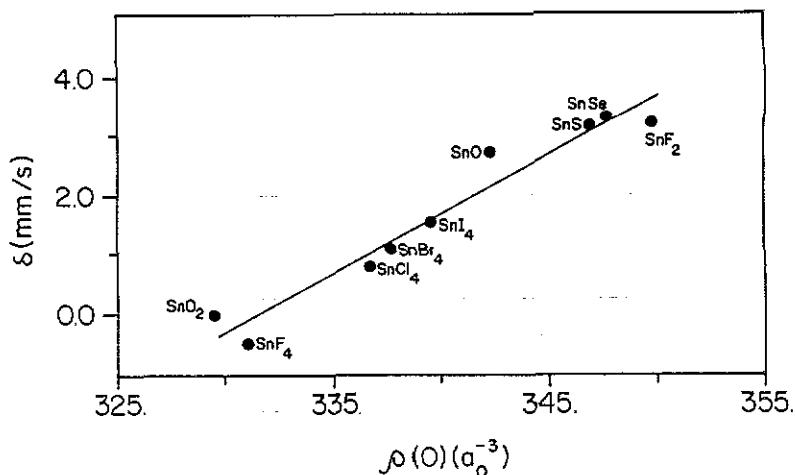


Figure 6. Correlation between isomer shifts  $\delta$  and electron densities  $\rho(0)$  ('shallow core' and valence) at the nucleus of the central Sn atom, for the largest clusters representing Sn(II) and Sn(IV) compounds.

In table 3 are also given the contributions to  $\rho(0)$  of the 'lone-pair' orbitals and compared with the total valence  $\rho(0)$ . It is seen that, owing to the distribution of the 5s charge between a large number of cluster orbitals in SnO, SnS and SnSe, the contribution of the 'lone-pair' orbitals to total  $\rho(0)$  is small for these compounds; in contrast, most of the 5s character of Sn<sub>c</sub> in SnF<sub>2</sub> is concentrated in the 58a 'lone-pair' orbital, which, accordingly, contributes 58% of the total valence  $\rho(0)$ .

It must be emphasized that the self-consistent method adopted here takes into account simultaneously all aspects of the chemical bonding that may influence the isomer shifts, such as covalency, charge transfer, potential distortion and changes in the shape of the wavefunctions due to the Pauli exclusion principle (sometimes called 'overlap distortion').

In figure 6 we present the correlation between  $\rho(0)$  ('shallow core' and valence) and experimental values of  $\delta$ . It is seen that an approximately linear correlation is obtained; by a least-squares fit of the points, the values  $\Delta R/R = (1.58 \pm 0.14) \times 10^{-4}$  (according to equation (8)) and  $\Delta\langle r^2 \rangle = (6.61 \pm 0.58) \times 10^{-3} \text{ fm}^2$  (according to equation (9)) were derived.

In figure 6 the results for the Sn(IV) compounds SnCl<sub>4</sub>, SnBr<sub>4</sub> and SnI<sub>4</sub> are also included; these were the subject of a previous publication [22], together with SnF<sub>4</sub> which, however, was represented by the smaller cluster [SnF<sub>6</sub>]. In this previous work, the DVM with a slightly different (less accurate) model potential was used, in which the coefficients of the expansion of the density  $\rho$  (equation (6)) were taken to be the Mulliken populations of the atomic orbitals. To make all results exactly comparable, calculations for SnCl<sub>4</sub>, SnBr<sub>4</sub> and SnI<sub>4</sub>, which form isolated tetrahedral units in the crystals and were thus represented by tetrahedral clusters, were repeated with the same model potential (equations (6) and (7)) as was adopted in the present calculations of Sn(II) and Sn(IV) compounds.

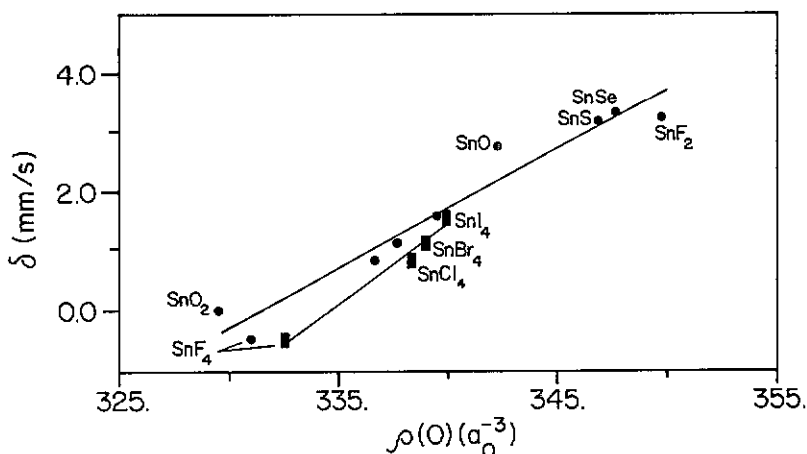


Figure 7. Correlation between isomer shifts  $\delta$  and electron densities  $\rho(0)$  at the nucleus of Sn: ●, present calculations; ■, calculations reported in [22], performed with a different model potential (see text).

In figure 7, the present linear correlation between  $\delta$  and  $\rho(0)$  is compared with that obtained from our previous investigation for SnF<sub>4</sub>, SnCl<sub>4</sub>, SnBr<sub>4</sub> and SnI<sub>4</sub>, in which a slightly different model potential was used and SnF<sub>4</sub> was represented by the smaller cluster [SnF<sub>6</sub>] [22]. The steeper inclination obtained for the straight line in this previous calculation resulted in a higher value for  $\Delta R/R$  ( $2.20 \times 10^{-4}$ ) than the present value of  $\Delta R/R$  ( $(1.58 \pm 0.14) \times 10^{-4}$ ). The present value is more reliable because of the use of an improved model potential and because both Sn(II) and Sn(IV) compounds have been included, covering a much wider range of isomer shift values.

The isomer shift calibration of <sup>119</sup>Sn has been the subject of investigation by other theoreticians. Early attempts were based on atomic models and resulted in a wide range of values proposed for  $\Delta R/R$  [23] (from  $-2.5$  to  $+3.6 \times 10^{-4}$ ). Semi-empirical calculations for Sn molecules were also employed [24]. Band-structure calculations for Sn metal and Sn compounds (SnO<sub>2</sub>, SnMg<sub>2</sub>, SnSb and SnTe) were performed [25] with the scalar-relativistic linear muffin-tin orbital (LMTO) method, for valence electrons only, resulting in  $\Delta R/R = (1.34 \pm 0.07) \times 10^{-4}$ . The same method was applied to investigate the pressure dependence of  $\delta$  measured in Sn metal [26], by performing calculations of  $\rho(0)$  for different lattice constants. The value of  $\Delta R/R$  derived ( $1.53 \times 10^{-4}$ ) is the closest that we found to the value reported here.

Other properties related to the electronic structures of the Sn(II) and Sn(IV) crystalline compounds investigated, such as densities of states and electric field gradients, will be reported in a forthcoming publication [27].

#### 4. Conclusions

The first-principles LD cluster calculations reported here have proved to be quite accurate in describing the linear correlation between isomer shifts and  $\rho(0)$  for Sn(II) and Sn(IV) solid compounds. Cluster size effects are found to be important, suggesting that caution must be exercised when selecting a cluster to investigate a property of a given crystal,

even when very localized as that studied here. Charges found are quite different from the formal +2 and +4. Of the four Sn(II) compounds considered, SnO, SnS and SnSe are very covalent and SnF<sub>2</sub> is ionic; for this last compound, the 'lone-pair' electrons are more localized.

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