First principles theoretical modeling of the Isomer shift of Mossbauer spectra
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Chapter 4

Calibration of $^{119}$Sn isomer shift

Synopsis

In the present chapter, the importance of the effects of relativity and electron correlation for accurate description of the isomer shift is demonstrated on the basis of the HF, MP2 and of the CCSD calculations on a series of iron ions. The isomer shift for the 23.87 keV M1 resonant transition in the $^{119}$Sn nucleus is calibrated with the help of ab initio calculations, the calibration constant $\alpha(^{119}$Sn) obtained from MP2 calculations ($\alpha_{MP2}(^{119}$Sn) = (0.091 ± 0.002) $a_0^{-3}$ mm/s) is in good agreement with the previously obtained values. The approach used in the calibration is applied to study the $^{119}$Sn isomer shift in CaSnO$_3$ perovskite under pressure. Comparison with the experimental results for the pressure range 0 GPa to 36 GPa shows that the linear response approach is capable of describing tiny variations of isomer shift with reasonable accuracy.

4.1 Introduction

The use of an empirical calibration constant $\alpha$ for the improvement of the correlation between experiment and theory is suggested in Chapter 3. In the present chapter, the linear response approach is applied
to the calibration of Mössbauer isomer shift of $^{119}$Sn nucleus. Tin compounds have been extensively studied with the use of the Mössbauer spectroscopy and there exists a plethora of the experimental data on the $^{119}$Sn isomer shift in various chemical environments [80–82].

In a number of previous studies, calibration constants $\alpha(^{119}\text{Sn})$ ranging from $0.17 \text{ a}_{\text{o}}^{-3} \text{ mm/s}$ [83] to $0.037 \text{ a}_{\text{o}}^{-3} \text{ mm/s}$ [84] have been deduced from the experimental and theoretical data. The most recent theoretical value of the $\alpha(^{119}\text{Sn})$ constant is $(0.092 \pm 0.002)\text{ a}_{\text{o}}^{-3} \text{ mm/s}$ as obtained in periodic density functional calculations of Svane et al. [82]. Hence accurate theoretical simulation of the experimental data over a wide range of chemical environments are used to obtain a theoretical value of the calibration constant $\alpha$, which is compared with the previously obtained values. In this chapter, a special emphasis is given on the use of systematically improvable \textit{ab initio} wave function methods and on the role of electron correlation effects for obtaining accurate theoretical results.

An independent test of the obtained calibration constant $\alpha(^{119}\text{Sn})$ is carried out for the theoretical simulations of the pressure dependence of the Mössbauer isomer shift in CaSnO$_3$ perovskite. It is our hope that the calibration of the $^{119}$Sn isomer shift on a representative set of compounds carried out with the use of accurate computational methods will help to improve the accuracy of interpretation of the experimental measurements.

The importance of including proper account of relativity and electron correlation in the calculations is demonstrated in a series of atomic calculations, for various oxidation states of iron atom.
4.2 Computational Details

The isomer shift of the Mössbauer spectrum is commonly related to the so-called contact density [5, 6, 12, 29], via Eqn. 3.1 ($\delta = \alpha (\bar{\rho}(a) - \bar{\rho}(s))$), in which $\alpha$ is the calibration constant which depends on the parameters of the nuclear $\gamma$-transition. However, the parameters of the nuclear $\gamma$-transition, such as the variation of the nuclear charge radius, are not known experimentally with sufficiently high accuracy, such that the direct determination of $\alpha$ is currently not possible. Presently, the most popular method of determination of the calibration constant is based on comparison of the theoretically estimated contact densities with the experimentally observed isomer shifts [5, 6, 12, 29, 30, 85]. In this calibration procedure, one uses a linear regression equation,

$$\delta = \alpha \bar{\rho} + b$$ \hspace{1cm} (4.1)

where the parameters $\alpha$ and $b$ are determined from the least squares fit. The electron contact densities near the nucleus are calculated according to Eqn. 2.44 (see Section 2.2.2 for details).

The calculations in this chapter are carried out both at HF and MP2 level. 21s15p11d2f basis set of Dyall [86] is used for Sn and for all other elements the augmented correlation consistent double-zeta (aug-cc-pVDZ) basis set of Dunning [74] is used. All basis sets are used in the uncontracted form.

In the current and following chapters, we employ embedded cluster approach to calculate the local electronic structure of solids. Within this approach, a cluster of atoms representing a structural unit of the crystalline solid is immersed in the Madelung potential of the rest of the crystal. The Madelung potential is modeled by a large array
of the point charges placed at the appropriate crystallographic positions. The magnitudes of the charges are determined from the natural bond order (NBO) analysis [87] of the respective cluster wave function calculated at the HF level. The co-ordinates of atoms in the clusters and of the point charges representing the Madelung field were obtained from the crystal structures generated with VESTA [88]. From our preliminary calculations we concluded that the inclusion of the Madelung potential of the crystal has relatively minor effect on the calculated contact densities (Eqn. 2.44) which is consistent with the conclusions of other works [29, 63]. However, because the clusters modeling the above solids are negatively charged, the embedding potential was added to compensate for the extra negative cluster charge.

The Sn compounds used in the present investigation are SnF$_4$, SnO$_2$, CaSnO$_3$, BaSnO$_3$, SnCl$_4$, SnS$_2$, SnBr$_4$, SnSe$_2$, SnI$_4$, SnO, SnS, SnSe and SnI$_4$. The isomer shift of these compounds ranges from -0.36 mm/s (SnF$_4$) to +4.06 mm/s (SnCl$_2$) (see Table 4.2). The sources of experimental values of each of these compounds are cited in Table 4.1. The crystal structures and the cluster geometries considered in the present work are explained below. The cluster geometries are represented in Figure 4.1.

SnF$_4$ [89] has a body-centered tetragonal structure. The considered cluster is [SnF$_6$]$^{2-}$, where the tin atom is surrounded by distorted octahedron of fluorine atoms (see Figure 4.1 (a)). The atomic positions are in the 14/mmm space group.

SnO$_2$ [90] has a rutile, tetragonal structure (P4$_2$/mnm). The cluster on which calculations are done is [SnO$_6$]$^{8-}$, where the tin atom is surrounded by a distorted octahedron of oxygen atoms (see Figure 4.1 (b)).

CaSnO$_3$ [91] and BaSnO$_3$ [91] have cubic structures (Pm$ar{3}$m). The
4.2. Computational Details

Figure 4.1: The cluster geometries used in the calculations, (a) \([\text{SnF}_6]^{2-}\) in SnF\(_4\) (b) \([\text{SnO}_6]^{8-}\) in SnO\(_2\) (c) \([\text{SnO}_6]^{8-}.8\text{M}^{2+}\), \text{M} = \text{Ca}/\text{Ba} in CaSnO\(_3\)/BaSnO\(_3\) respectively (d) \([\text{SnO}_6]^{8-}.8\text{Ca}^{2+}\) in CaSnO\(_3\) perovskite (e) \([\text{SnX}_4]\), X = Cl/Br in SnCl\(_4\)/SnBr\(_4\) respectively (f) \([\text{SnE}_6]^{8-}\), E = S/Se in SnS\(_2\)/SnSe\(_2\) respectively (g) \([\text{SnI}_4]\) in SnI\(_4\) (h) \([\text{Sn}_4\text{O}_{14}]^{20-}\) in SnO (i) \([\text{SnE}_3]^{1-}\), E = S/Se in SnS/SnSe respectively (j) \([\text{SnCl}_7]^{5-}\) in SnCl\(_2\).