Concerning the calibration of the Mössbauer isomer shift from data on the chemical changes of the electron-capture probabilities

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It is explained why the calibration constants of the scale of the Mössbauer isomer shift, determined from data on the chemical changes $\Delta\lambda/\lambda$ of the probabilities of electron capture by ^{52}Fe and ^{125}I nuclei, differ strongly from those determined by other methods. The cause of the difference is the influence exerted on $\Delta\lambda/\lambda$ by the chemical changes of the exchange and overlap corrections to the probabilities of electron capture, and by the chemical changes of the electron binding energies, which was not taken into account in the interpretation of the $\Delta\lambda/\lambda$ data.

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1. The problem of determining the calibration constants of the scale of the Mössbauer isomer shift (of the coefficients of proportionality of the isomer shift to the chemical change of the electron density in the vicinity of the nuclei), although used for the solution of many experimental methods,[1] has so far been solved only qualitatively or semi-quantitively (only the signs and tentative values of the calibration constants are known) for even the most widely used Mössbauer nuclei. The isomer shift δ is connected with the change $\Delta\rho(0)$ of the electron density $\rho(0)$ in the region of the nucleus by the relation[2]

$$\delta={}^2/_3\pi Ze^2\Delta\langle r^2\rangle\Delta\rho(0), \tag{1}$$

where Z is the atomic number, e is the elementary charge, and $\Delta\langle r^2\rangle=\langle r^2\rangle^*-\langle r^2\rangle$ is the difference between the mean squared radii of the nuclei in the excited and ground states. The determination of the calibration constant reduces therefore to a determination of the nuclear factor $\Delta\langle r^2\rangle$. This calls for the measurement of δ and for an independent determination of $\Delta\rho(0)$ for the same pair of chemical compounds.

The differences between the values of $\Delta\langle r^2\rangle$ determined by different methods frequently exceed the experimental errors. The differences are particulary large in the values of $\Delta\langle r^2\rangle$ determined recently for Mössbauer transitions in the nuclei ^{57}Fe (Ref. 3) and ^{127}I and ^{129}I (Ref. 4) using $\Delta\rho(0)$ values obtained from data on the chemical changes $\Delta\lambda/\lambda$ of the probabilities λ of electron capture. There are also differences between the values of $\Delta\langle r^2\rangle$ determined on the basis of $\Delta\lambda/\lambda$ data obtained in experiments with different isotopes.[4,5] This is illustrated in Table I, which lists,

TABLE I. Values of $\Delta\langle r^2\rangle$ for Mössbauer nuclei.

Mössbauer nucleus	$\Delta\langle r^2\rangle\cdot 10^3$, fm^2		Nucleus with which $\Delta\lambda/\lambda$ was measured
	Tentative[6] or "best"[7] value	Determined from $\Delta\lambda/\lambda$	
^{57}Fe	−14.3 [6]	−33±3 [3]	^{52}Fe
^{127}I	−10 [7]	−23 *±6 [4]	^{125}I
		−12±2 [5]	^{123}I
^{129}I	13 [7]	31 *±7 [4]	^{125}I
		18±3 [5]	^{123}I

*These values of $\Delta\langle r^2\rangle$ were recalculated (they correspond to the values of $\Delta R/R$ cited in Ref. 4).

besides these values of $\Delta\langle r^2\rangle$, certain tentative[6] and best[7] values obtained for $\Delta\langle r^2\rangle$ by other methods.

It is shown in the present paper that the cause of these difference is the failure of the authors of Refs. 3–5 to take into account important factors on which $\Delta\lambda/\lambda$ depends.

2. For electron capture stemming from allowed transitions and from first-forbidden non-unique transitions (these are the only transitions of practical interest at present), $\Delta\lambda/\lambda$ can be expressed as[8,9]

$$\frac{\Delta\lambda}{\lambda}=\sum_x\Delta[(Q-\varepsilon_x)^2B_x\rho_x(0)]\Big/\sum_x[(Q-\varepsilon_x)^2B_x\rho_x(0)], \tag{2}$$

where x denotes the electron subshell, and the summation is only with the values of x corresponding to s and p electrons (with the s electrons making the main contribution). $Q-\varepsilon_x$ is the energy carried away by the neutrino when an electron is captured from the x shell, Q is the total energy released in the capture, and ε_x is the energy required to excite the atom and the system associated with it, equal practically in most decay acts to the electron binding energy in the daughter atom. B_x are correction factors that take into account the exchange and overlap effects in electron capture.[10-12] $\rho_x(0)$ are the electron densities in the region of the nucleus. In accordance with (2), $\Delta\lambda/\lambda$ can be represented as a sum of three terms, $(\Delta\lambda/\lambda)_{\Delta\rho}$, $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$, and $(\Delta\lambda/\lambda)_{\Delta B}$, which result from the changes in $\Delta\rho(0)$, $\Delta\varepsilon_x$, and ΔB_x:

$$\frac{\Delta\lambda}{\lambda}=\left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta\rho}+\left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta\varepsilon}+\left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta B}. \tag{3}$$

To determine $\Delta\rho(0)$ from the $\Delta\lambda/\lambda$ data it is necessary to subtract from the measured value of $\Delta\lambda/\lambda$ the values $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$ and $(\Delta\lambda/\lambda)_{\Delta B}$. In a number of papers[3-5] $\Delta\lambda/\lambda$ is identified with $(\Delta\lambda/\lambda)_{\Delta\rho}$.

3. The contribution made to $\Delta\lambda/\lambda$ by the change of the electron binding energies depends on the energy Q. It can be estimated from the simple relation[8,9]

$$(\Delta\lambda/\lambda)_{\Delta\varepsilon}=-2\Delta\varepsilon_K/(Q-\bar{\varepsilon}), \tag{4}$$

where $\Delta\varepsilon_K$ is the change of the binding energy ε_K of the K electrons (in the daughter atom), and $\bar{\varepsilon}$ is the average binding energy of the electrons of the orbits in which

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the capture takes place ($\bar{\varepsilon}$ is somewhat smaller than ε_K).

Estimates of $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$ for ^{125}I in various iodine ions are given in Ref. 8. Their values are of the same order ($\approx 10^{-4}$–10^{-3}) as the measured[4] values of $\Delta\lambda/\lambda$. In the case of ^{123}I, for which the energy Q is much higher [$Q(^{123}\mathrm{I}) = 1.04$ MeV, Ref. 13] than that of ^{125}I[$Q(^{125}\mathrm{I}) = 142.5$ keV, Ref. 13], the values of $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$ are, in accordance with (4), smaller by a factor 9. In the case of ^{52}Fe [$Q(^{52}\mathrm{Fe}) = 1.726$ MeV, Ref. 13], even the maximum possible chemical changes $(\Delta\lambda/\lambda)_{\rho\varepsilon}$ are negligibly small ($\sim 10^{-5}$ for $\Delta\varepsilon_K \approx 10$ eV, much less than the measurement error of $\Delta\lambda/\lambda$).

Only the neglect of the effect of chemical changes of the electron binding energies can explain the contradictory results obtained for $\Delta\langle r^2\rangle$ by using the $\Delta\lambda/\lambda$ data for ^{123}I and ^{125}I (see Table I). The published[4,5] values of $\Delta\langle r^2\rangle$ are in fact the values of the expression

$$\Delta\langle r^2\rangle \left[\left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta\rho} \Big/ \left(\frac{\Delta\lambda}{\lambda}\right)\right] = \Delta\langle r^2\rangle \left[\left(\frac{\Delta\lambda}{\lambda}\right) - \left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta B} - \left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta\varepsilon}\right] \Big/ \frac{\Delta\lambda}{\lambda},$$

which can differ greatly for two isotopes of the same chemical element only because the values of $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$ are different if the differences between the energies Q are large. To determine $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$ [by formula (4)] we need the values of $\Delta\varepsilon_K$, which are unknown. However, by ascribing the difference the values of

$$\Delta\langle r^2\rangle \left[\frac{\Delta\lambda}{\lambda} - \left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta B} - \left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta\varepsilon}\right] \Big/ \frac{\Delta\lambda}{\lambda},$$

obtained on the basis of the $\Delta\lambda/\lambda$ data for ^{123}I and ^{125}I solely to the difference between the values of $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$ and taking into account the relation (4) and the concrete values of Q for two isotopes and the value of $\bar{\varepsilon}$, we can obtain the values of the ratio $(\Delta\lambda/\lambda)_{\Delta} / [(\Delta\lambda/\lambda)_{\Delta\rho} + (\Delta\lambda/\lambda)_{\Delta B}]$. For ^{125}I and ^{123}I this ratio is -0.44 ± 0.18 and -0.076 ± 0.032 respectively. Allowance for this contribution of the changes of $(\Delta\lambda/\lambda)_{\Delta\varepsilon}$ in an approximation in which the exchange effects and their chemical changes are neglected [if $(\Delta\lambda/\lambda)_{\Delta B} = 0$], leads to the following values of $\Delta\langle r^2\rangle$:

$$\Delta\langle r^2\rangle = -(13\pm 2)\cdot 10^{-3}\ \mathrm{fm}^2 \text{ for } ^{127}\mathrm{I}, \tag{5}$$

$$\Delta\langle r^2\rangle = +(17\pm 3)\cdot 10^{-3}\ \mathrm{fm}^2 \text{ for } ^{129}\mathrm{I}. \tag{6}$$

4. To estimate the contribution made to the total $\Delta\lambda/\lambda$ changes by the $(\Delta\lambda/\lambda)_{\Delta B}$ changes we need some data on the electron structures of the atoms in the concrete chemical compounds. Calculations[14] show that this contribution is small in those cases when the chemical bond does not affect the valence s electrons (it amounts to approximately 7% for $Z = 33$ and should be even less for iodine), in which case $(\Delta\lambda/\lambda)_{\Delta B}$ compensates somewhat for the change $(\Delta\lambda/\lambda)_{\Delta\rho}$. This contribution can be very large if the atoms of the compared chemical compounds have different numbers of valence s electrons. At any rate, allowance for the changes $(\Delta\lambda/\lambda)_{\Delta B}$ should lead to a decrease of the nuclear factors $\Delta\langle r^2\rangle$ (5) and (6). As a result of the foregoing, the values of $\Delta\langle r^2\rangle$ (5) and (6) for Mössbauer transitions in the nuclei ^{127}I and ^{129}I must be regarded as the upper limit of the true values. If the best values[7] (see Table I) are indeed closest to the true ones, then the deviations of the values of (5) and (6) from the best ones can be regarded as a quantitative measure of the change $(\Delta\lambda/\lambda)_{\Delta B}$:

$$\frac{(\Delta\lambda/\lambda)_{\Delta B}}{(\Delta\lambda/\lambda)_{\Delta\rho}} = \frac{\Delta\langle r^2\rangle}{\Delta\langle r^2\rangle^*} - 1, \tag{7}$$

where $\Delta\langle r^2\rangle$ is the true value, and $\Delta\langle r^2\rangle^*$ are the values in (5) and (6). In the case considered,

$$\left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta B} \Big/ \left(\frac{\Delta\lambda}{\lambda}\right)_{\Delta\rho} = -0.24 \tag{8}$$

(on the average, on the basis of the $\Delta\lambda/\lambda$ data obtained by others[4,5]; a comparison of the iodine nuclei in concrete compounds may yield a different value).

5. In the case of iron, $\Delta\rho(0)$ was determined in Ref. 3 by assuming that for the ^{52}Fe decay mode via electron capture $(\Delta\lambda/\lambda)/[\Delta\rho(0)/\rho(0)] = 1$. Calculations of $\Delta\lambda/\lambda$ [in accord with formula (2)], with account taken of the changes of the exchange and overlap factors B_x as functions of the electron-shell configuration, shows that this ratio depends strongly on the electron configurations of the compared atoms or ions, and ranges from -0.08 to $+1.25$ for different iron ions.[14]

To determine $\Delta\rho(0)$ and $\Delta\langle r^2\rangle$ from the $\Delta\lambda/\lambda$ data for ^{52}Fe we must estimate the values of $(\Delta\lambda/\lambda)_{\Delta B}$ for the concrete pairs of compounds. If the entire difference between the two values of $\Delta\langle r^2\rangle$ for ^{57}Fe, listed in Table I, is ascribed to failure to take $(\Delta\lambda/\lambda)_{\Delta B}$ into account, then it follows from (7) that in this case

$$(\Delta\lambda/\lambda)_{\Delta B}/(\Delta\lambda/\lambda)_{\Delta\rho} = -0.57. \tag{9}$$

In such a case this value can be regarded as the average experimental value for the two pairs of compounds investigated in Ref. 3. For concrete compound pairs, this ratio can be entirely different.

Some change in the obtained $\Delta\langle r^2\rangle$ can be due to the chemical influence on the strong (56% according to Ref. 3) positron mode of the ^{52}Fe decay. The chemical changes of the positron-decay probability (not observed so far) should be much smaller than the changes of the electron-capture probabilities.[15] These changes, however, should tend to balance each other.[16] As a result, the values of $\Delta\langle r^2\rangle$ calculated using the $\Delta\lambda/\lambda$ data without allowance for this influence may be somewhat overestimated.

6. The following conclusions can be drawn:

1) It does not follow at all from the previously published[3,4] measured chemical changes of the probabilities of electron capture by ^{52}Fe and ^{125}I electrons that the values of $\Delta\langle r^2\rangle$ for Mössbauer transitions in ^{57}Fe, ^{127}I, and ^{129}I are much larger than the presently assumed tentative values of $\Delta\langle r^2\rangle$.

2) The values of $\Delta\lambda/\lambda$ measured with the ^{52}Fe nucleus[3] serve as an experimental confirmation of the chemical changes of the exchange and overlap corrections to the electron-capture probabilities.

4) The determination of the values of $\Delta\rho(0)/\rho(0)$ on the basis of the measured values of $\Delta\lambda/\lambda$ is a rather complicated problem, since it is always necessary to investigate and take into account the effect of the changes ΔB_x and $\Delta\varepsilon_x$ on $\Delta\lambda/\lambda$.

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