⁵⁷Fe Isomer Shifts and the Problem of Calibration

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The ⁵⁷Fe isomer shift calibration problem is discussed, and critical comments concerning the paper "⁵⁷Fe Isomer Shift Calibration Experiment" by Daniel et al. (1985) are given. We consider $-\langle \Delta r^2 \rangle = (20 \pm 3) \cdot 10^{-3} \text{ fm}^2$ at the moment as the most reliable estimate for the change of nuclear radius during gamma absorption; this value has been derived by measuring changes in isomer shift δ and calculating corresponding changes in electron contact density $\varrho(0)$ according to $\Delta \delta = C \langle \Delta r^2 \rangle \Delta \varrho(0)$.

A reliable calibration of the isomer shift δ is the prerequisite for deriving contact densities $\rho(0)$ from Mössbauer spectra. It is therefore important to design experiments with the aim to measure directly the change of nuclear radius $\langle \Delta r^2 \rangle$ during gamma resonance absorption. Such experiments have been performed for 57Fe on the basis of life time variations in the electron capture decay of ⁵²Fe [1] or on the basis of conversion electron spectroscopy with ⁵⁷Co(⁵⁷Fe) sources [2]. However, the results, which have been obtained with these two methods, $-\langle \Delta r^2 \rangle = (33 \pm 3) \cdot 10^{-3} \, \text{fm}^2$ [1] and $-\langle \Delta r^2 \rangle < 9$ $\cdot 10^{-3}$ fm² [2], respectively, do not agree at all. Other authors, including ourselves, strived for this goal by measuring changes in δ and calculating corresponding changes in o(0) [3, 4]:

$$\Delta \delta = C \left\langle \Delta r^2 \right\rangle \Delta \varrho(0) \,. \tag{1}$$

If δ is given in mm s⁻¹, $\langle \Delta r^2 \rangle$ in 10⁻³ fm², and $\varrho(0)$ in a_0^{-3} , the constant C takes the value 0.011 for ⁵⁷Fe. From the combined experimental ($\Delta \delta$) and calculational ($\Delta \varrho(0)$) procedure we have derived $\langle \Delta r^2 \rangle$ for a large variety of iron-containing compounds, i.e. $-\langle \Delta r^2 \rangle = (20 \pm 3) \cdot 10^{-3}$ fm² [4–6].

Due to its importance it is desirable to have a widely accepted isomer shift calibration. In our view there are serious drawbacks which cause us to

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question the value $-\langle \Delta r^2 \rangle < 9 \cdot 10^{-3} \text{ fm}^2$ (at 80% confidence) [2], due to the following reasons:

(i) The absolute value of the Fe 4s contact density $\rho_{4s}(0)$ was obtained in [2] from the experimental ratio α_{4s}/α_{3s} and the calculated relativistic Fe 3s value ($\rho_{3s}(0) \sim 180 a_0^{-3}$), i.e.

from
$$\alpha_{4s}/\alpha_{3s} = 0.061 \pm 0.005$$
 the value
 $\varrho_{4s}(0) = (10.98 \pm 0.90) a_0^{-3}$ for ⁵⁷Fe/Au, (2a)

and

from
$$\alpha_{4s}/\alpha_{3s} = 0.17 \pm 0.10$$
 the value (2b)
 $\varrho_{4s}(0) = (30.6 \pm 18.0) a_0^{-3}$ for ⁵⁷Fe/graphite.

With the experimental isomer shifts 0.65 mm s^{-1} for ${}^{57}\text{Fe/Au}$ and 0.25 mm s^{-1} for ${}^{57}\text{Fe/graphite}$ and the values (2a, b) we derive from (1)

$$-\langle \Delta r^2 \rangle = 1.85 \cdot 10^{-3} \, \text{fm}^2$$
.

Comparison with the upper limit of $9 \cdot 10^{-3}$ fm² given in [2] shows that the error margin is about $7 \cdot 10^{-3}$ fm², which means that the confidence grows only slowly when one raises the upper limit. By exhausting the full uncertainty of (2 a, b) on arrives at

$$-\Delta \langle r^2 \rangle \lesssim 50 \cdot 10^{-3} \, \mathrm{fm}^2$$
,

without even having considered any uncertainties of isomer shifts, because they were not reported in [2]!

(ii) The values for $\varrho_{4s}(0)$ in (2a) and (2b) are larger than the corresponding value $\varrho_{4s}(0) = 8.36 a_0^{-3}$ for Fe⁰ (3d⁶ 4s²) as derived from Dirac-Fock calculations [4], the same calculations which yield $\varrho_{3s}(0) \sim 180 a_0^{-3}$ from above. This implies that the isomer shifts of ⁵⁷Fe/Au and ⁵⁷Fe/graphite should be even more negative than that of Fe⁰ in solid noble gas ($\delta_{\alpha-Fe} \sim -0.75 \text{ mm s}^{-1}$ [7]), which is by far not the case.

(iii) The value for $\langle \Delta r^2 \rangle$ was estimated by Daniel et al. [2] on the basis of (1) by assuming $\Delta \varrho(0) = \Delta \varrho_{4s}(0)$. But this assumption is not necessarily satisfied, as shown in a conversion electron study of $\varrho_{4s}(0)$ of Fe-impurity atoms in transition and noble metals [8]. In fact, we have found from electronic structure calculations [4, 5] that core contributions to $\Delta \varrho(0)$ can be significantly larger than $1 a_0^{-3}$.

In conclusion, we consider $-\langle \Delta r^2 \rangle = (20 \pm 3) \cdot 10^{-3} \text{ fm}^2$ at the moment as the most reliable estimate, because we do not regard the result

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