An experimental method for a precise determination of gamma-ray energies with semiconductor detectors

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Abstract

This paper presents a method for determining gamma-ray energies with a precision similar to that of the primary standards. The method consists of both an experimental procedure which employs Ge detectors, and the statistical treatment of data. An actual example with ¹⁵⁶Gd β⁺⁻ decay illustrates its use.

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1. Introduction

The first Ge detectors that became available produced great advances in nuclear spectroscopy because of the significant resolution improvement over scintillator detectors, thus enabling the interpretation of very complex nuclear level schemes. The energy resolution also allowed a precise determination of the peak location, and consequently of the gamma-ray energy. When the development of these detectors began, however, the gain and zero stability of the Analog-to-Digital Converters (ADC) and amplifiers were not good enough to assure high accuracy in the energy determination. Nowadays, with the improvement of electronic data acquisition systems, together with the computer ability to store and analyze many spectra, it is possible to determine peak-channel numbers with a precision of one part in 10⁷. Thus, gamma-ray energies with a precision similar to that of the primary gamma-ray standards may be achieved with Ge detectors [1].

We present in this paper an experimental method which uses Ge detectors to determine gamma-ray energies relative to those from primary standards, with the precision and accuracy of the latter. The procedure described here takes into account both the restrictions imposed by the instruments and those from the method of analysis. We took into account, under some assumptions, possible effects due to the lack of linearity of the ADC, and due to peak distortions caused by the simultaneous measurement of sources.

It turned out that the data analysis was more complex than the usual procedure of fitting a single polynomial. It required all correlations between the data to be determined and taken into account both to calculate standard deviations, and to perform a chi-square test with the measured energies.

2. Measuring gamma-ray energies – single spectrum

2.1. Calibration

Although electronic devices are currently very stable, still peak-channel numbers change with time much more than the standard deviation of the corresponding parameter, usually determined by the least-squares method [2]. Then, a convenient procedure to determine gamma-ray transition energies consists of a simultaneous measurement of gamma-rays from the sample and from a calibration standard [3]. All the mathematical and notational details of the least-squares method, used throughout this paper, are given in the appendix.

The calibration data set can be represented by

\[ \{(C_i, E_i), \ i = 1,N\} \]

where for each standard gamma-ray energy \(E_i\), the peak-channel number \(C_i\) is obtained by fitting procedures. The
usual calibration function is the polynomial

\[ E(C) = a_1 + a_2 C + \cdots + a_n C^{n-1}. \]  

(1)

Hence, the experimental data and the parameters are related by

\[ \begin{pmatrix} E_1 \\ E_2 \\ \vdots \\ E_N \end{pmatrix} = \begin{pmatrix} C_1 & \cdots & C_1^{n-1} \\ 1 & C_2 & \cdots & C_2^{n-1} \\ \vdots & \vdots & \ddots & \vdots \\ 1 & C_N & \cdots & C_N^{n-1} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} + \begin{pmatrix} e_1 \\ e_2 \\ \vdots \\ e_N \end{pmatrix}, \]

(1a)

where \( e_i \) is the error in \( E_i \). The equation can be written as follows:

\[ E = CA_0 + e, \]

(1b)

analogous to Eq. (A.1).

To obtain the least-squares estimate of the calibration function parameters \( A \), we must calculate the covariance matrix \( V \), comprised of two independent terms, as follows:

\[ V = V_e + V_c, \]

(2)

where \( V_e \) is the covariance matrix of the standard energies (it should not be diagonal [4]), and \( V_c \) is the covariance matrix of \( E \), which results from the statistical fluctuations in the determination of peak-channel numbers. In the example of Section 5, we will assume \( V_e \) to be diagonal, due to the lack of information about the covariances between gamma-ray energies in the calibration standard. However, as indicated below, the experimental procedure does take into account non-vanishing covariances, as they should be whenever known.

The covariance matrix \( V_c \), which takes into account the uncertainty in the peak-channel numbers, is given by (see Eq. (A.10))

\[ V_c \simeq \text{PV} \text{P}', \]

(3)

where \( V_c \) is the covariance matrix of the peak-channel numbers, and \( P \) is a diagonal matrix with elements (Eq. (A.11))

\[ P_i = \sum_{\eta=2}^{N} (\eta - 1)a_\eta C_\eta^{n-2} \]

(4)

since each energy depends only on the location of its corresponding peak in the spectrum.

The calculation of both \( P \) and \( V_c \), however, warrants some additional explanations. The parameters \( A \) are needed to calculate \( P \), and therefore, also \( V \). Thus, this is an iterative least-squares fit, despite the linearity of the calibration function on the parameters \( A \). Nevertheless, only the first-degree term of the fitted polynomial contributes appreciably to the matrix \( V_c \), and is easily determined with great precision. All that is needed to solve this problem is a preliminary calculation to estimate the first-degree coefficient of the polynomial.

The diagonal elements of \( V_c \) have two components. The first one is the variance \( \sigma_i^2 \) of the peak-channel numbers, determined from the least-squares fit of a Gaussian function with exponential tail, plus a quadratic polynomial background, and a step function [5]. The second component takes into account the effects of lack of linearity of the ADC, which adds an uncertainty to the peak-channel number. The differential non-linearity (a measure of the lack of linearity) is \(<1\%\) for the Wilkinson-type ADC used in the experiment described in Section 5. We calculate \( (V_c)_{ii} \), subject to further verification (see Section 5), as follows:

\[ (V_c)_{ii} = \sigma_i^2 \simeq \sigma_i^2 + 0.0033^2. \]

(5)

assuming that the overall effect in the peak-channel number (determined by the least-squares fit) corresponds just to an increase in its variance. The added dispersion of 0.0033 channels is an empirical estimate, which changes the variances only for peaks with high number of counts, where \( \sigma_i^2 \) is of the same order of magnitude (0.0033). The spectra should be measured for relatively short periods, in order to achieve a good fit \((\chi^2/d.f. \approx 1)\), which would enable us to use \( \sigma_i^2 \), as determined by the least-squares method. Only completely resolved peaks were used in this calibration procedure. Consequently, the peak-channel numbers \( C_i \) are statistically independent, that is, \( (V_c)_{ij} = 0 \) for \( i \neq j \).

For most practical cases, when the coefficients of \( E(C) \) of order greater than 1 are negligible, and peak-channel numbers of gamma rays from the standards are uncorrelated, the covariance matrix (3) becomes

\[ (V_c)_{ij} \simeq \delta_{ij} \cdot \sigma_i^2, \]

where \( \delta_{ij} \) is the Kronecker delta, and \( \sigma_i^2 \) is the fitted value for the first degree term of the function \( E(C) \).

Summarizing, for gamma-ray energy calibrations, \( E \) is the vector formed by the gamma-ray energies, \( C \) is the design matrix given by the peak-channel numbers of the fitted peaks (Eq. (1a)), and the parameters can be calculated using Eq. (A.4) as shown below:

\[ \bar{A} = (C^t V^{-1} C)^{-1} C^t V^{-1} E, \]

(6)

where \( V \) is the covariance matrix constructed as shown above (Eqs. (2), (3) and (5)). The covariance matrix of \( \bar{A} \) is given by Eq. (A.5)

\[ V_{\bar{A}} = (C^t V^{-1} C)^{-1}. \]

(7)

Since \( V \) depends on the fitted parameters, it has to be calculated iteratively. The procedure, however, converges rapidly because \( \bar{A} \) is easily determined with sufficient precision to give a good estimate of \( V \). The variable

\[ \chi^2 = (E - C \bar{A})^t V^{-1} (E - C \bar{A}) \]

(8)

has a chi-square distribution with \( N - v \) degrees of freedom and should be used as a test for the goodness of the fit.
2.2. Interpolation

Let us consider the calibration procedure described above. The energies \( D = (D_1, D_2, \ldots, D_i, \ldots, D_n)' \) of a set of gamma rays with peak channel numbers \( B = (B_1, B_2, \ldots, B_i, \ldots, B_n)' \) can be interpolated using

\[
D = B\hat{A},
\]

where \( B \) is a matrix similar to matrix \( C \) given by Eq. (1a), but built with the values \( B_i \).

The covariance matrix of \( D \) is

\[
V_D = BV_B B' + \sigma_B^2 V_B,
\]

where \( V_b \) is the covariance matrix of the peak-channel number \( B \). The first term on the right-hand side of Eq. (10), which corresponds to the covariance propagation from \( A \) to \( D \), estimates the statistical fluctuation in the energies due to the uncertainties in the calibration parameters. The second term on the right-hand side corresponds to the variance propagation of the fitted peak-channel numbers into \( D \), analogous to Eqs. (3) and (5).

The covariance matrix \( V_D \) is non-diagonal due to the common dependence of every energy on the same parameters. This fact shows, as stated above, that the covariances between gamma-ray energies simultaneously measured do not vanish. These covariances must be taken into account in the calibration procedures, in statistical tests, and, of course, for the propagation of variances.

3. Measuring gamma-ray energies – many spectra

3.1. Calibration

A measurement of a sample source using a single calibration standard usually does not give enough precision for a large energy range. Mixing many calibration sources is not a solution because one obtains a very complex spectrum. Therefore, we propose to measure several spectra, each one with one calibration standard and the sample source, and to determine the energies as averages of the interpolated values in the various spectra. This procedure has the advantage of reducing any systematic error produced in a peak-channel number by distortions due to a specific calibration standard, since each combination sample source – calibration standard will have a different spectrum shape.

Generalizing the results from Section 2 to the measurement of several spectra, we define \( E^{(i)} = (E_1^{(i)}, E_2^{(i)}, \ldots, E_n^{(i)})' \) as the gamma-ray energies used to calibrate the detector system in the \( i \)th measurement, \( (C_1^{(i)}, C_2^{(i)}, \ldots, C_n^{(i)})' \) the respective fitted peak-channel numbers, and \( A^{(i)} = (a_1^{(i)}, a_2^{(i)}, \ldots, a_i^{(i)})' \) the parameters of the calibration curve in the same spectrum, where \( i = 1, 2, \ldots, l \) refer to the \( l \) different spectra. The experimental data and the parameters are related by

\[
\left( \begin{array}{c} E_1^{(i)} \\ E_2^{(i)} \\ \vdots \\ E_n^{(i)} \\ \end{array} \right) = \left( \begin{array}{ccc} C_1^{(i)} & 0 & \cdots & 0 \\ 0 & C_2^{(i)} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & C_n^{(i)} \\ \end{array} \right) \left( \begin{array}{c} A_1^{(i)} \\ A_2^{(i)} \\ \vdots \\ A_n^{(i)} \\ \end{array} \right) \]

or

\[
E^{(i)} = C^{(i)} A^{(i)} + \epsilon^{(i)}.
\]

and can be compared with Eqs. (1a) and (1b).

The vector \( E^{(i)} \) is formed by the juxtaposition of vectors \( E_1^{(i)} \), represented in a partitioned form in Eq. (11a); \( C^{(i)} \) is a matrix formed by the rectangular matrices \( C^{(i)} \), each one with a structure similar to that of matrix \( C \) in Eq. (1a), and represented in partitioned form in Eq. (11a); \( A^{(i)} \) is the vector formed by the juxtaposition of vectors \( A^{(i)} \).

The covariance matrix \( V^{(i)} \) of \( E^{(i)} \), given below, is a generalization of Eq. (2):

\[
V^{(i)} = \sigma_{E}^2 V_{E} + \sigma_{E}^2 V_{E},
\]

where \( V^{(i)} \) is given by Eq. (3), and the elements of \( V^{(i)} \) are

\[
(V^{(i)})_{\alpha\beta} = \text{cov}(E_\alpha, E_\beta).
\]

It should be noticed that \( \text{cov}(E_\alpha, E_\beta) = \sigma_{E}^2 \) if \( E_\alpha \) and \( E_\beta \) refer to the same gamma-ray calibration energy \( E \), irrespective of whether they were measured in the same or in different measurements; otherwise, \( \text{cov}(E_\alpha, E_\beta) = 0 \). \( \sigma_{E} \) is the standard deviation of the gamma-ray energy \( E \).

The fitted parameter \( A^{(i)} \) and their covariance matrix \( V_{A^{(i)}} \), are given by Eqs. (A.4) and (A.5), replacing \( X \) by \( C^{(i)} \), \( Y \) by \( E^{(i)} \), and \( V \) by \( V^{(i)} \). The chi-square test can be performed by using the variable \( \chi^2 \) defined in Eq. (A.6), and the same substitution mentioned above. Such \( \chi^2 \) variable obeys a chi-square distribution with a number of degrees of freedom equal to the difference between the number of data points in \( E^{(i)} \) and the number of fitted parameters in \( A^{(i)} \).

3.2. Interpolation

The interpolated energies are given by

\[
\left( \begin{array}{c} D_1^{(i)} \\ D_2^{(i)} \\ \vdots \\ D_n^{(i)} \\ \end{array} \right) = \left( \begin{array}{ccc} B_1^{(i)} & 0 & \cdots & 0 \\ 0 & B_2^{(i)} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & B_n^{(i)} \\ \end{array} \right) \left( \begin{array}{c} A_1^{(i)} \\ A_2^{(i)} \\ \vdots \\ A_n^{(i)} \\ \end{array} \right)
\]

for each \( i = 1, 2, \ldots, l \)
or
\[ D^{(L)} = B^{(L)} \cdot A^{(L)}. \]  
(14b)

\[ D^{(L)} \] is the vector whose elements are the energies determined from all the measurements, and \( B^{(L)} \) is a matrix which contains the appropriate powers of the peak-channel numbers. Using Eq. (10), the covariance matrix of the fitted energies becomes
\[
V_{D^{(L)}} - B^{(L)} (B^{(L)})^T + \begin{pmatrix}
(\hat{\sigma}_D)^2 V_{B^{(L)}} & 0 \\
0 & (\hat{\sigma}_D)^2 V_{B^{(L)}}
\end{pmatrix}.
\]  
(15)

Since \( D^{(L)} \) contains several fitted energies corresponding to the same transition, it is necessary to average their values for each transition. Let us call \( D \) the vector containing each energy transition once. The final step in the analysis can be accomplished by using the least-squares method with the appropriate design matrix \( X \) given by
\[
(X h)_n = \frac{\partial (D^{(L)})_n}{\partial (D)_n},
\]  
(16)

where the partial derivative is equal to 1 if \((D^{(L)})_n \) and \((D)_n \) refer to the same transition, and equal to 0 otherwise. The estimate of the energies, given by Eq. (A.4), is
\[
D = (X'(V_{D^{(L)}})^{-1} X)^{-1} X'(V_{D^{(L)}})^{-1} D^{(L)},
\]  
(17)

with covariance matrix \( V_D \), calculated by using Eq. (A.5), as
\[
V_D = (X'(V_{D^{(L)}})^{-1} X)^{-1}.
\]  
(18)

The variable
\[
\chi^2 = (D - X \cdot D^{(L)})'(V_{D^{(L)}})^{-1} (D - X \cdot D^{(L)}),
\]  
(19)

has a chi-square distribution with a number of degrees of freedom equal to the difference between the number of gamma-ray energies in \( D' \) and the number of level energies in \( G \).

4. Level energies

When the gamma-ray energies given by \( D \) and its covariance matrix \( V_D \) are known, it is possible to determine the level energies by the least-squares method. First, it is necessary to define a transition energy vector \( D' \) that is equal to \( D \) plus the recoil energies. The covariance matrix of \( D' \) is well approximated by the covariance matrix of \( D \), since the variances of the recoil energies are negligibly small. To establish the relation between transition and level energies, let us call \( G_n \) the \( n \)th level energy. Then, each gamma-ray energy may be given by
\[
(D')_n = G_n - G_s.
\]  
(20)

The method described above was applied to the measurement of gamma-ray energies from \( ^{159}\text{Gd} \) decay [6]. In this section we describe with more detail the individual procedures.

Following the procedure given in Section 3.1, we performed eight calibration measurements using standard sources of \( ^{133}\text{Ba} \) (four spectra) and \( ^{152}\text{Eu} \) (four spectra) simultaneously with the \( ^{159}\text{Gd} \) sample. The aim of this study was to detect weak gamma rays from \( ^{159}\text{Gd} \) \( \beta^- \) decay. To obtain enough counting statistics, four spectra of 24 h each were taken with the \( ^{159}\text{Gd} \) source alone. Fig. 1 shows how the experiment was scheduled.

A least-squares fit to a second degree polynomial calibration function was performed as described in Section 3.1. The final results were the vector \( A^{(L)} \) and the corresponding covariance matrix \( V_A^{(L)} \). The gamma-ray energies of \( ^{133}\text{Ba} \) and \( ^{152}\text{Eu} \), from 53 to 1112 keV, were taken from the tables of Ref. [7], and not corrected for the current values of the fundamental constants. The 964 keV transition of \( ^{152}\text{Eu} \) was discarded due to a disagreement in the energy values between various references [8]. The reduced chi-square value of the fit was 1.10, with 68 degrees of freedom.

The energies of the most prominent and well resolved full energy peaks from \( ^{159}\text{Gd} \) \( \beta^- \) decay were interpolated using the procedure given in Section 3.2. Their values are

Fig. 1. Spectra measurement time table for the study of the \( ^{159}\text{Gd} \) decay.

The appropriate design matrix for the least-squares fit is calculated by
\[
(X')_n = \frac{\partial (D')_n}{\partial (G)_n},
\]  
(21)

It is a matrix with elements equal to 1, -1, or 0, and specific to each individual level scheme. The estimated level energies, their covariance matrix, and \( \chi^2 \) may be calculated by Eqs. (A.4), (A.5), and (A.6), respectively, substituting \( X, Y, V, \) and \( A \) by \( X', D', V_D, \) and \( G \), respectively. The number of degrees of freedom is equal to the difference between the number of gamma-ray energies in \( D' \) and the number of level energies in \( G \).

5. Application to \( ^{159}\text{Gd} \) decay

The method described above was applied to the measurement of gamma-ray energies from \( ^{159}\text{Gd} \) \( \beta^- \) decay [6]. In this section we describe with more detail the individual procedures.

Following the procedure given in Section 3.1, we performed eight calibration measurements using standard sources of \( ^{133}\text{Ba} \) (four spectra) and \( ^{152}\text{Eu} \) (four spectra) simultaneously with the \( ^{159}\text{Gd} \) sample. The aim of this study was to detect weak gamma rays from \( ^{159}\text{Gd} \) \( \beta^- \) decay. To obtain enough counting statistics, four spectra of 24 h each were taken with the \( ^{159}\text{Gd} \) source alone. Fig. 1 shows how the experiment was scheduled.

A least-squares fit to a second degree polynomial calibration function was performed as described in Section 3.1. The final results were the vector \( A^{(L)} \) and the corresponding covariance matrix \( V_A^{(L)} \). The gamma-ray energies of \( ^{133}\text{Ba} \) and \( ^{152}\text{Eu} \), from 53 to 1112 keV, were taken from the tables of Ref. [7], and not corrected for the current values of the fundamental constants. The 964 keV transition of \( ^{152}\text{Eu} \) was discarded due to a disagreement in the energy values between various references [8]. The reduced chi-square value of the fit was 1.10, with 68 degrees of freedom.

The energies of the most prominent and well resolved full energy peaks from \( ^{159}\text{Gd} \) \( \beta^- \) decay were interpolated using the procedure given in Section 3.2. Their values are
shown on the ninth column of Table 1. The following remarks about the partial results of the interpolated energies for each calibration spectrum are necessary for a better understanding of the procedure. These energies are presented in Table 1, columns 1–8. Notice that the acquisition of several independent spectra using the same calibration source reduces the standard deviations. For each calibration spectrum the standard deviations of the interpolated energies are largely independent of the specific spectrum and they fall in the range 2.5 eV (e.g., 58 and 364 keV gamma rays) to 50 eV for 855 keV gamma ray. After averaging, the deviations become even smaller. Neglecting covariance effects, one would expect the standard deviation of the average to be equal to that obtained in the single calibration spectrum divided by \(\sqrt{N}\), for those peaks that are present in all the spectra (like the 58 and 364 keV gamma rays). For peaks that appear in four spectra only (e.g., 855 keV gamma ray) one would expect a reduction of 0.5 (i.e. \(1/\sqrt{4}\)) in the standard deviation value for a single spectrum. The precision of the average values are in agreement with this argument (1.0–1.5 eV for 58 and 364 keV gamma rays, and 50 eV for the \(855\) keV gamma ray). This argument breaks down only when the uncertainties in the primary standards are larger than those in the interpolated energies.

A gamma-ray spectrum with high counting statistics of the \(^{159}\)Gd source was obtained by summing four individual spectra. These spectra first were gain matched, then added up by using the method described in Ref. [9]. The energy calibration for this combined spectrum was performed according to the procedure described in Section 2, using as calibration energies the 11 previously interpolated energies of the \(^{159}\)Gd source. A second degree polynomial fit produced a reduced chi-square value of 0.86, with 9 degrees of freedom. The final energies and covariances of all gamma-ray transitions following the \(^{159}\)Gd \(\beta^+\) decay were obtained by employing the method described in Section 2. The energies of the excited states of \(^{159}\)Tb, daughter of \(^{159}\)Gd, were evaluated by applying the procedure given in Section 4, which resulted in a reduced chi-square value of 0.92, with 11 degrees of freedom.

The striking sensitivity of the level energy fit to the gamma-ray energies and their covariances is remarkable. Due to the cascade-crossover constraints, implicit in the model given by the set of Eqs. (20), the reduced chi-square value most likely will not fall within the acceptance region if the gamma-ray energies and their covariances have incorrect values. This also occurs when there is a misplacement of a gamma-ray transition. Two examples, which illustrate the sensitivity of the method, are shown in Table 2. The first and second columns contain the final deduced gamma-ray energies for \(^{159}\)Gd \(\beta^+\) decay, and the respective absolute residues relative to the standard deviations, respectively. The third and fourth columns show the same information, but the corrections given by Eq. (5) were not included. In this case the high chi-square value suggests an underestimation of the deviations. When the ADC lack of linearity effects were taken into account, the relative residues of the gamma-ray energies (given with a precision of about 1 eV) became smaller. The fifth column shows an example where a misplacement of a 480 keV transition in the level scheme between levels with energies of 617.63 and 137.51 keV became apparent by its large relative residue (see Ref. [6] for more details about the level scheme). We stress that the conclusions deduced from these results are meaningful only if the covariances are used in the calculations.

### 6. Conclusions

The experimental method for measuring gamma-ray energies using Ge detectors described here may produce
Table 2
Gamma-ray energies and absolute residues of the transitions assigned to $^{152}\text{Gd}$ $\beta^-$ decay calculated with different assumptions about the ADC’s lack of linearity, and the placement of the 480 keV transition in the level scheme. The absolute residue is calculated by the absolute value of $(E_{\text{exp}} - E_{\text{calc}})/\sigma_{\text{exp}}$, where $E_{\text{exp}}$ and $\sigma_{\text{exp}}$ are the interpolated gamma-ray energy and its standard deviation, respectively, and $E_{\text{calc}} = E_i - E_f$ is the energy difference between the two fitted levels, corrected for the recoil of the nucleus. The absolute residues presented in the fifth column were calculated using the energy values of the first column.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Absolute Residue $^a$</th>
<th>Energy (keV)</th>
<th>Absolute Residue $^a$</th>
<th>Absolute Residue $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.0000 (22)</td>
<td>1.7</td>
<td>57.9999 (15)</td>
<td>2.8</td>
<td>1.7</td>
</tr>
<tr>
<td>79.513 (3)</td>
<td>1.4</td>
<td>79.5132 (18)</td>
<td>2.0</td>
<td>1.4</td>
</tr>
<tr>
<td>137.515 (5)</td>
<td>1.8</td>
<td>137.515 (4)</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>210.783 (3)</td>
<td>1.8</td>
<td>210.7828 (24)</td>
<td>2.7</td>
<td>1.8</td>
</tr>
<tr>
<td>226.0408 (18)</td>
<td>1.0</td>
<td>226.0406 (11)</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>237.341 (5)</td>
<td>0.2</td>
<td>237.341 (4)</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>273.62 (12)</td>
<td>0.1</td>
<td>273.62 (12)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>274.163 (19)</td>
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<td>274.163 (18)</td>
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<td>0.1</td>
</tr>
<tr>
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<td>305.5491 (11)</td>
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<td>0.6</td>
</tr>
<tr>
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<td>348.2806 (10)</td>
<td>1.1</td>
<td>0.2</td>
</tr>
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<td>363.5428 (10)</td>
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<td>0.1</td>
</tr>
<tr>
<td>349.84 (6)</td>
<td>—</td>
<td>349.84 (5)</td>
<td>—</td>
<td>4.7</td>
</tr>
<tr>
<td>536.730 (12)</td>
<td>0.3</td>
<td>536.730 (11)</td>
<td>0.6</td>
<td>0.3</td>
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<tr>
<td>559.623 (6)</td>
<td>0.7</td>
<td>559.622 (5)</td>
<td>1.4</td>
<td>0.5</td>
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<td>580.080 (6)</td>
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<td>580.080 (5)</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>616.233 (18)</td>
<td>0.5</td>
<td>616.233 (17)</td>
<td>0.7</td>
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<td>0.9</td>
<td>617.615 (7)</td>
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<td>0.5</td>
<td>674.26 (4)</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>753.74 (6)</td>
<td>0.1</td>
<td>753.74 (6)</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>854.947 (20)</td>
<td>0.7</td>
<td>854.945 (19)</td>
<td>1.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

$^a$ The sum of the squared absolute residues is only a rough approximation of the chi-square value, since the energies $E_{\text{exp}}$ are correlated. Eq. (19) should be used to calculate chi-square, giving the value quoted in the last line of the table.

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Appendix

A.1. The least-squares method in matrix notation

Let us assume that a physical quantity can be represented by a function $f(x, A)$, where $x$ represents a vector with $m$ independent variables, and $f$ is a linear function of $v$ unknown parameters represented by the vector $A$. Let us also assume that the quantity was measured for $N$ values of the independent variables, obtaining $Y_i = f(x_i, A_0) + \epsilon_i, i = 1, 2, \ldots, N$, where $A_0$ is the true (and unknown) value of the parameter vector, and $\epsilon_i$ stands for the experimental error of $Y_i$. The experimental data and the parameters are related by the following equation:

$$ Y = XA_0 + \epsilon, \quad (A.1) $$

where $Y$ is a $(N \times 1)$ vector, $A_0$ is a $(v \times 1)$ vector parameter of true values, $\epsilon$ is a $(N \times 1)$ vector of unknown errors, and $X$ is the $(N \times v)$ design matrix. This matrix does not depend on $A_0$, and it contains all of the model dependence on $x$. The error $\epsilon$ in this equation refers to the difference between the experimental and the true value of a quantity. Only mathematical expectations of this error may be estimated.

The following two assumptions are needed to calculate the least-squares estimate of $A_0$: the data are unbiased,

$$ \langle \epsilon_i \rangle = 0, \quad (A.2) $$

and

$$ \sum_i \epsilon_i = 0 \quad (A.3) $$

where $\sum_i \epsilon_i$ is the sum of the squared experimental errors.

The least-squares estimate of $A_0$ is given by

$$ A_0^\text{ls} = (X^T X)^{-1} X^T Y, \quad (A.4) $$

which is the ordinary least-squares solution. The precision of this solution is given by

$$ A_0^\text{ls} = (X^T X)^{-1} X^T Y, \quad (A.5) $$

where $\sigma^2$ is the variance of the errors $\epsilon_i$.

Results with a precision comparable to that of the primary energy standards. The procedure is not difficult, but requires to perform several steps. The data analysis makes use of the least-squares technique, which produces results with minimum variance.
and the covariance matrix \( \mathbf{V} \), defined by
\[
V_{ii} = (\bar{e}_i \cdot \bar{e}_i),
\]
is known. Expectation values are represented by \( (\cdot) \).

Eq. (A.2) implies the absence of systematic errors in the observations. Eq. (A.3) defines, for \( i = j \), the variance of \( Y_i \), and for \( i \neq j \), the covariance between \( Y_i \) and \( Y_j \).

The least-squares estimate in matrix notation \([10, 11]\) is given by
\[
\hat{\mathbf{A}} = (\mathbf{X}^\mathsf{T} \mathbf{V}^{-1} \mathbf{X})^{-1} \mathbf{X}^\mathsf{T} \mathbf{V}^{-1} \mathbf{Y},
\]
where the superscript \( \mathsf{T} \) indicates transposition. The covariance matrix of the estimates is given by
\[
\mathbf{V}_{\hat{\mathbf{A}}} = (\mathbf{X}^\mathsf{T} \mathbf{V}^{-1} \mathbf{X})^{-1}
\]
Eqs. (A.4) and (A.5) may also be obtained by minimizing the function
\[
Q = \sum_i \left( y_i - f(x_i, \mathbf{A}) \right)^2 / \sigma_i^2
\]
for the case where the covariance matrix \( \mathbf{V} \) is diagonal, i.e., \( V_{ii} = \sigma_i^2 \), and \( V_{ij} = 0 \) for \( i \neq j \). The equations given above are the simplest ones that include statistical correlations in the data. The following quantity
\[
\chi^2 = (\mathbf{Y} - \mathbf{X} \mathbf{A})^\mathsf{T} \mathbf{V}^{-1} (\mathbf{Y} - \mathbf{X} \mathbf{A})
\]
has a probability density function of chi-square with \( N - v \) degrees of freedom if the joint probability density function of \( Y_i \) is a \( N \)-dimensional Gaussian. This quantity should be used to assess the quality of the fit.

The estimate given by Eq. (A.4) is unbiased, which follows from its structure and the unbiasedness of the data expressed by condition (A.2). Among the estimation functions \( \hat{\mathbf{A}}(y) \) linear in \( y \), Eq. (A.4) gives the estimate with minimum variance. These optimum properties do not depend on the shape of the data probability density function. The proof of these properties may be found in Refs. [10, 11].

### A.2. Variance propagation in matrix notation

Let us assume that we have an experimental data set consisting of \( \mu \) random variables that define a vector \( \mathbf{x} = (x_1, x_2, \ldots, x_\mu)^\mathsf{T} \). We will represent by \( \text{cov}(x_i, x_k) \) the covariance between \( x_i \) and \( x_k \), and define \( \text{cov}(x_i, x_k) = \text{var}(x_i) \). The true value of \( x_i \) will be represented by \( x_{i0} \), and the set of random variables defines the vector \( \mathbf{x}_0 = (x_{10}, x_{20}, \ldots, x_{\mu0})^\mathsf{T} \). Let us consider now random variables \( z_i \) and \( z_j \), which statistically depend on the random variables \( x_{i0} \), \( x_{j0} \), with values given by the functions \( z_i(\mathbf{x}) \) and \( z_j(\mathbf{x}) \), respectively. The true value of \( z_i \), \( z_j \), is approximately given by
\[
z_{i0} \equiv z_i(\mathbf{x}_0),
\]
and the covariance between \( z_i \) and \( z_j \), by
\[
\text{cov}(z_i, z_j) \cong \sum_{\eta=1}^{\mu} \frac{\partial z_i}{\partial x_{i\eta}} \bigg|_{x=x_{i0}} \text{cov}(x_{i\eta}, x_{j\eta}) \frac{\partial z_j}{\partial x_{j\eta}} \bigg|_{x=x_{j0}} \text{cov}(x_{i\eta}, x_{j\eta}).
\]

The variances may be calculated by using the same expression with \( i = j \).

Eqs. (A.8) should be represented in a matrix form to conveniently determine all the variances and covariances of a set of \( M \) random variables functions \( z = (z_1(\mathbf{x}), z_2(\mathbf{x}), \ldots, z_m(\mathbf{x}))^\mathsf{T} \). We define \( \mathbf{V}_z \) as the covariance matrix of the random variables
\[
(V_z)_{jk} = \text{cov}(z_j, z_k),
\]
and the covariance matrix between the functions by
\[
(V_z)_{jk} = \text{cov}(z_j, z_k).
\]
The relation between the covariance matrices of \( \mathbf{x} \) and \( \mathbf{z} \) is given by
\[
\mathbf{V}_z \cong \mathbf{Z} \mathbf{V} \mathbf{Z}^\mathsf{T},
\]
where
\[
(Z)_{jk} = \frac{\partial z_i}{\partial x_{i\eta}} \bigg|_{x=x_{i0}}.
\]
If \( z_i(\mathbf{x}) \) were linear functions of \( \mathbf{x} \), then Eqs. (A.7) and (A.10) would be exact, and \( \mathbf{V}_z \) would be independent of the vector \( \mathbf{x}_0 \). Since we use experimental values of \( \mathbf{V}_z \), only approximate estimates of \( \mathbf{V}_z \) will be obtained.

### References