Increased accuracy of the binding energy of K– and L–subshell electrons in krypton from re-analysis of experimental data: importance for determination of the neutrino mass

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Analyzing thoroughly K and L X–ray transition energies, results of a former L–shell photoabsorption study and subM binding energies from photoelectron and optical spectroscopy, we determined the following electron binding energies in gaseous krypton: 14 327.26 (4) eV for the K–shell and 1 921.4(3), 1 731.91(3) and 1 679.21(3) eV for L_1–, L_2– and L_3–subshells, respectively. These accurate values of electron binding energies are important for energy calibration of the next generation tritium β–decay experiment KATRIN with sub-eV sensitivity for the electron neutrino mass.

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1 Introduction

Measurement of the neutrino rest mass is one of the main tasks of contemporary physics with far reaching consequences for cosmology and particle physics. At the time being, the most sensitive model-independent method is a precise measurement of the energy spectrum of electrons emitted in the tritium β–decay:

$$^3\mathrm{H} \rightarrow\ ^3\mathrm{He} + \mathrm{e}^- + \tilde{\nu}_e \qquad (1)$$

where $\tilde{\nu_e}$ is the electron antineutrino. Due to the ^{3}H decay into three particles the electron spectrum is continuous and its uppermost part near to the endpoint energy E_0 of 18.6 keV is sensitive to the neutrino mass m_ν. In principle, both E_0 and m_ν can be determined from measured β–spectrum. Regardless great effort lasting several decades, only upper limits for m_ν were derived until now, the best ones being about 2 eV [1, 2].

The international collaboration KATRIN [3] founded in 2001 is developing a β–ray spectrometer of unprecedented parameters and aims at improving sensitivity to neutrino mass by one order of magnitude up to 0.2 eV. It was shown recently

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[4] that the analysis of the last tens of eV of the tritium β–spectrum could yield correct values of m_ν even if the spectrometer energy scale would suffer from a bias of several tens of eV. Of course, such a fit would yield a wrong value of E_0. At the same time, comparison of the fitted endpoint energy with the mass difference $\Delta M(^3\mathrm{H},^3\mathrm{He})$ that was established independently by means of mass spectroscopy, represents an important check of correct treatment of measured β–spectrum. The value of $\Delta M(^3\mathrm{H},^3\mathrm{He})$ is known with 1.7 eV standard deviation [5] and improvement up to one order of magnitude is expected [6]. Thus an absolute calibration of the spectrometer energy scale is one of important tasks of the KATRIN collaboration.

Predecessors searching for the neutrino mass in β–spectra often calibrated their β–spectrometers with conversion electrons of known energy, e.g. those emitted from the krypton K–shell during internal conversion of the 32 keV nuclear transition in ^{83m}Kr. Energy of these electrons, E_{kin}, is about 17.8 keV (not far from the tritium endpoint energy) but it is known with an accuracy of 2 eV [7], not sufficient for the KATRIN purposes. For ^{83m}Kr in gaseous form, we obtain

$$E_{kin} = E_\gamma + E_{\gamma,rec} - E_b(vac) - E_{e,rec} \tag{2}$$

Here, E_γ is the γ–ray energy, $E_b(vac)$ is the binding energy of K–shell electrons related to the vacuum level, $E_{\gamma,rec} = 0.0067$ eV is the energy of the recoil atom after γ–ray emission and $E_{e,rec} = 0.120$ eV is the energy of the recoil atom after conversion electron emission.

A possible way to increase precision of E_{kin} is to accurately measure the energy of the 32 keV γ–ray transition in ^{83}Kr and also to improve knowledge of the binding energy of K–shell electrons in gaseous krypton. These quantities enter into an expression (2) for kinetic energy of calibrating conversion electrons. The L_2 and L_3 conversion electrons of this transition would allow extending the calibration up to 30 keV.

Determination of the inner-shell binding energies with about 0.1 eV uncertainty is not an easy task and much larger scatter is often found among the results of various investigators. In addition, the agreement between theoretical and experimental K– and L–transition and absorption edges is rarely better than 1 eV (see e.g. the most recent comprehensive evaluation of Deslattes et al. [8]. Survey of tabulated data in Table 1 demonstrates rather unsatisfactory situation for the K–shell and L–subshell electron binding energies of krypton.

In the present work, we attempt to increase accuracy of the K–shell and L–subshell electron binding energies in krypton combining appropriate K and L X-ray transition energies with L– and M–subshell binding energies.

2 Experimental

2.1 Methods

There are two main ways for determination of the binding energies. The first one is the direct measurement of the photoelectron line by an electron spectrometer using monochromatized photon beams of very well known energies (emission lines

in the VUV and X–ray energy range, synchrotron radiation over the entire photon energy range). This method has the advantage of requiring the measurement of only one parameter in the electron analyzer but suffers from some uncertainty in the spectrometer work function [12, 13, 14]. Measuring some previously determined calibration lines [13, 14] could solve the problem.

The second method is to accurately determine transition energies between appropriate subshells by X–ray emission spectroscopy [8] and to measure lower binding energies of outer shells that are more amenable to accurate measurements [15, 16]. One could also use X–ray photoabsorption spectroscopy when discrete excitation transitions of inner electrons to specific excited states can be measured [17, 18]. This approach, applying in some cases the core-equivalent approximation [18], provides rather accurate inner-shell energies.

2.2 Previous results for krypton

Using alternatively electron energy-loss spectroscopy and electrostatic electron spectrometer, King et al. [16] measured the binding energies of the krypton M–subshells with an accuracy of 20–25 meV. Codling and Madden [15] also determined these energies from the limit of photoabsorption Rydberg series with an accuracy of 70 meV. Johansson [13] and Siegbahn et al. [14] measured the binding energies of the L-subshells using a magnetic electron spectrometer calibrated using the ionization energies of the outer shells of several noble gases. These ionization energies are known with high accuracy from optical spectroscopy [19]. Krause [12] measured the binding energies of the L-subshells using an electrostatic spectrometer.

Finally, the binding energies of the L–subshells and K–shell were determined by Wuilleumier [17], using the bremsstrahlung emitted by an X–ray tube, and by Breinig et al. [18] by means of monochromatized synchrotron radiation, respectively. These photoabsorption studies were carried out with gaseous krypton. Using the core equivalent approximation, the binding energies of the L–subshells and K–shell were determined in the following way. In both cases, the authors obtained, experimentally or theoretically, the energy differences between the core level (with which the edge is associated) and several normally unoccupied bound states to which electron dipole transition can lead. The core level binding energy was then deduced by linking the obtained energy differences to the vacuum level. For this purpose, the above mentioned equivalent core approximation was employed to estimate the excited state energies in the noble gas (atomic number Z) from the known energies of optical levels in the neighboring alkali element (Z+1) [19].

Table 2 shows the binding energies of electrons in the K– through M_5–subshells of krypton measured by various authors with the described methods. The results of Krause for the L–subshells [12], based on the photoelectron spectroscopy, do not refer to the vacuum level but to the Fermi level. The author estimated that this difference, connected with the energy calibration of his spectrometer, lowered his binding energies by about 4 eV [17].

3 Evaluation of the electron binding energies

3.1 L–subshells

In this work, we applied two ways to determine the L_2 and L_3 binding energies in krypton. Firstly, we utilized the photoabsorption data [17]. We assumed that after an inner 2p- electron of krypton was picked-up into an excited atomic orbital, the electronic core relaxed "immediately" in such a way that the potential seen by the excited electron was equivalent to the potential produced by a (Z+1) nuclear charge screened by Z core electrons. This assumption was supported by the ratio of the lifetime, τ, of the excited state to the atomic period, T, of the electron on its excited orbital. For 2p-electrons in krypton, τ/T is about 400. Thus it was reasonable to think that the core–hole excited atomic state had enough time to fully relax and that the energies of the excited electrons in the resonant lines could be approximated by the values of the binding energies of the outer electron in the next alkali– metal, the rubidium. Relevant data are exhibited in Table 3.

In order to account for an uncertainty of this application of the equivalent core approximation, we enlarged the standard deviations of weighted means for the L_2 and L_3 binding energies in Table 3 to 0.1 eV. This corresponds to systematic error of 0.04 or 0.08 eV in dependence on linear or quadratic addition of statistical and systematic uncertainties. Thus our values derived from measurement [17] of the L–absorption edges are $E_b(L_2) = 1731.8(1)$ eV and $E_b(L_3) = 1679.3(1)$ eV. As for the L_1–subshell, only a broad L_1 absorption edge without any resonance line was observed [17] and its energy was determined to be 1921.4(3) eV.

Secondly, we determined the L_2 and L_3 binding energies by combining accurately measured wavelengths of X–ray transitions with appropriate electron binding energies for atomic shells with a higher principal quantum number. In our case,

$$E_b(L_2) = E_X(L_2M_4) + E_b(M_4) \tag{3}$$

$$E_b(L_3) = E_X(L_3M_5) + E_b(M_5), \tag{4}$$

where the obvious notation of the two X–ray transitions corresponds to historical ones, $L\beta_1$ and $L\alpha_1$. We took the krypton X–ray transition energies from the most recent evaluation of Deslattes et al. [8]: $E_X(L_2M_4) = 1636.876(21)$ eV and $E_X(L_3M_5) = 1585.411(26)$ eV. (Note that all X–ray transition energies for krypton we used in our work are results of direct measurements by Mooney as cited in [8].)

The binding energies $E_b(M_4) = 95.04(2)$ eV and $E_b(M_5) = 93.79(2)$ eV are weighted averages of values from refs. [13, 15, 16] based on optical and electron spectroscopy. The values [14] having larger uncertainties of 0.2 eV agree with all other determinations. We did not include them into our weighted averages since they were superseded by more accurate results [13] from the same laboratory. From Eqs.(3) and (4), we obtained $E_b(L_2) = 1731.92(4)$ eV and $E_b(L_3) = 1679.21(3)$ eV.

The weighted means of the two determinations described in this section yielded our final values of the electron binding energies in gaseous krypton: $E_b(L_2) = 1731.91(3)$ eV and $E_b(L_3) = 1679.21(3)$ eV.

3.2 K–shell

To improve accuracy of the binding energy of K-shell electrons in gaseous krypton we utilized the relations

$$E_b(\mathrm{K}) = E_X(\mathrm{KL_3}) + E_b(\mathrm{L_3}), \tag{5}$$

$$E_b(\mathrm{K}) = E_X(\mathrm{KL_2}) + E_b(\mathrm{L_2}), \tag{6}$$

$$E_b(\mathrm{K}) = E_X(\mathrm{KM_3}) + E_b(\mathrm{M_3}), \tag{7}$$

$$E_b(\mathrm{K}) = E_X(\mathrm{KM_2}) + E_b(\mathrm{M_2}). \tag{8}$$

The X–ray transition energies exhibiting accuracy of 0.05 – 0.11 eV were taken from the evaluation of Deslattes et al. [8], while the electron binding energies of Siegbahn et al. [14] for the subshells $\mathrm{M_2}$ and $\mathrm{M_3}$ (accurate to 0.2 eV) were employed. For the L–subshell binding energies we preferred to utilize results of our present work since the values of ref. [14] have 0.5 eV uncertainties.

The four $E_b(\mathrm{K})$ determinations according to Eq.(5) to (8) yielded very consistent results: 14327.21(6), 14327.33(7), 14327.22(22) and 14327.16(23) eV. Their weighted mean, $E_b(\mathrm{K}) = 14327.26(4)$, with $\chi^2 = 1.85$ for 3 degrees of freedom, is our final result for the K–shell.

4 Conclusion

In this work, we determined binding energies of K– and L–subshell electrons in gaseous krypton with substantially better accuracy than quoted by previous investigators. Our results will make more accurate the energy calibration of the KATRIN β–ray spectrometer [3] searching for the neutrino mass. Precision of our experimental values may stimulate a further theoretical study for this particular case of this many-electron atom with all closed shells. The present work demonstrates again that substantial improvement of the electron binding energies for inner atomic shells can be reached when the existing precise X–ray transition energies [8] are complemented with sufficiently accurate electron binding energies for the outer atomic shells.

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Table 1. Tabulated binding energies (eV) of the K–shell and L–subshell electrons in krypton

Reference	K	L_1	L_2	L_3
Bearden and Burr [9] eval.	14 327.6(8)	1921.0(6)	1727.2(5)	1674.8(6)
Deslattes et al. [8] eval.	14 327.19(13)	1920.4(12)	1730.90(50)	1679.07(39)
Deslattes et al. [8] theor.	14 328.06(20)	1925.49(79)	1732.49(36)	1680.06(31)
Present work	14 327.26(04)	1921.4(3)	1731.91(3)	1679.21(3)

The values of Bearden and Burr [9] from 1967 were reproduced in tabulations of Sevier [10] from 1979 and Firestone [11] from 1996.

Table 2. Measured binding energies in krypton (eV)

Reference	K	L_1	L_2	L_3	M_2	M_3	M_4	M_5
Codling and Maden [15]							95.04(7)	93.83(7)
Krause et al. [12]		1921.2(8)	1727.2(6)	1674.8(6)				
Wuilleumier [17]		1924.1(1)	1731.80(6)	1679.30(6)				
Siegbahn [14]		1924.6(8)	1730.9(5)	1678.4(5)				
Johansson et al. [13]					222.2(2)	214.4(2)	94.9(2)	93.7(2)
King et al. [16]						214.55(1.5)		93.80(10)
Breinig et al. [18]	14327.2(8)						95.038(25)	93.788(20)
Deslattes [8]	14327.19(13)							

Measurements are given in chronological order

Table 3. Krypton resonance lines and binding energies for L_2– and L_3–subshells (eV)

		L_3–subshell		L_2–subshell	
Resonant excitation transition	Optical level of Rb	Resonant line energy	Binding energy	Resonant line energy	Binding energy
$[..]2p^6[..]4p^6\ ^1S_0 \rightarrow [..]2p^5[..]4p^6 5s\ ^1P_1$	5s – 4.18	1675.1(1)	1679.28(11)	1727.6(1)	1731.78(11)
$[..]2p^6[..]4p^6\ ^1S_0 \rightarrow [..]2p^5[..]4p^6 4d\ ^1P_1$	4d – 1.78	1677.4(1)	1679.18(11)	1729.9(1)	1731.68(11)
$[..]2p^6[..]4p^6\ ^1S_0 \rightarrow [..]2p^5[..]4p^6 6s\ ^1P_1$	6s – 1.68	1677.7(1)	1679.38(11)	1730.2(1)	1731.88(11)
Weighted mean			1679.28(6)		1731.78(6)

$[..]2p^6[..]4p^6\ ^1S_0$ stands for $[1s^22s^2]2p^6[3s^23p^63d^{10}4s^2]4p^6\ ^1S_0$

$[..]2p^5[..]$ stands for $[1s^22s^2\,]2p^5(^2P_{3/2})[3s^23p^63d^{10}4s^2]$ and
$[1s^22s^2\,]2p^5(^2P_{1/2})[3s^23p^63d^{10}4s^2]$ in the cases of L_3– and L_2–subshell, respectively.