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Review

Measuring a Mass: The Puzzling History of an Elusive Particle

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Abstract: Since Pauli's hypothesis of their existence in 1930, neutrinos never ceased to bring into play novel ideas and to add new pieces of physics in the whole picture of fundamental interactions. They are only weakly interacting and, at odds with Standard Model's predictions, have a mass less than one millionth of the electron mass, which makes the investigation of their properties very challenging. The issue of the measurement of neutrino's rest mass gained a wider and wider consensus since its discovery through neutrino oscillations in 1998. Various neutrino sources are available for experiments, ranging from nuclear collisions of cosmic rays in the Earth atmosphere and supernova explosions to neutrino beams produced by accelerators and power reactors. These suggest different approaches to the experimental detection and measurement of the absolute value of the neutrino mass. In this paper, we retrace the intriguing story of this endeavor, focusing mainly on direct mass determination methods. The puzzling issue of the nature of massive neutrinos is addressed as well with explicit reference to the phenomenon of double beta-decay as a viable experimental tool to discriminate between Dirac's and Majorana's nature.

Keywords: direct neutrino mass measurements; orbital electron capture; Dirac vs. Majorana; neutrinoless double beta-decay

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1. Introduction

The existence of neutrino as an unknown neutral light particle was hypothesized for the first time in 1930 by Wolfgang Pauli[1] in an attempt to get rid of the problem of energy non-conservation in β-decay as inferred from the continuous energy spectrum of β-electrons observed in experiments. His proposal was also expected to provide a solution to the related issue of the wrong spin and statistics of several nuclei, for example the ^{14}N nucleus,[2] in a period in which even the failure of quantum mechanics at nuclear scales was a common belief among scientists.[3] Two years later, in 1932, James Chadwick's discovery of the neutron [5,6] shed new light on the nuclear structure and paved the way to Enrico Fermi's successful theory of β-decay, which was indeed a masterpiece [7–10].

Fermi's work built upon Pauli's neutrino hypothesis and the assumption that nuclear constituents are only neutrons and protons. He made a clever use of analogy with the electromagnetic case while using a second quantization framework, as vividly expressed at the beginning of his paper:

> [...] in order to understand that β-emission is possible, we want to try to construct a theory of the emission of lightweight particles from the nucleus in analogy with the theory of emission of light quanta from an excited atom by the usual radiation process. In radiation theory, the total number of light quanta is not constant. Light quanta are created when they are emitted from an atom, and are annihilated when they are absorbed ([10], p. 1151).

Hence, β-decay was modeled as a process in which the total number of electrons and neutrinos was not constant so that they could be created and annihilated, while neutron and proton were two states of the same particle, the nucleon [11]. This requirement resulted in a Hamiltonian function describing the process, implementing both the transition from a neutron to a proton accompanied by the creation of an electron–neutrino pair and the inverse transition (proton to neutron with the annihilation of an electron and a neutrino). Furthermore, according to the chosen framework, the neutrino and antineutrino were different particles and the corresponding picture was that of Dirac's neutrino. A few years later, in 1937, E. Majorana [12] would have developed a new picture based on the opposite assumption that the neutrino and the antineutrino are indeed the same particle! Fermi made the further assumption of a contact interaction between the vector currents of heavy (n, p) and light particles (e, ν), respectively, and provided an estimate of the coupling constant g as 4×10^{-50} erg cm^3. Finally, he discussed the dependence of the shape of the continuous β-spectrum on the rest mass of the neutrino and suggested a criterion to determine it: a vertical or horizontal slope of the spectrum near its endpoint (i.e., its high energy part) as the signature of a nonzero or zero mass, respectively, [7–10]. Then, from a comparison with empirical curves, he was able to infer that a neutrino had a mass much smaller than the electron mass. Fermi's conclusions prompted the prediction of the existence of other processes involving *weak currents*, such as the *inverse* β*-decay* $\overline{\nu}_e + p \to n + e^+$, whose cross section was estimated by H. A. Bethe and R. Peierls [13] as the upper limit $\sigma < 10^{-44}$ cm^2, i.e., an extremely small value.[4] Clearly, at this stage, only the electron neutrino was known, the muon and tau flavors would have been predicted later.

Fermi's results, confirmed independently by Perrin [14], marked the beginning of a race toward the experimental detection of the neutrino, which looked very challenging. Since the 1930s, various strategies and apparatus were devised in order to find the elusive particle, ranging from the radiochemical method pioneered by H. R. Crane [15,16] and B. Pontecorvo[5] [17] to a convenient choice of the source (a nuclear reactor) as well as the detector (liquid scintillators [18–20] and photomultipliers). All these efforts culminated in the successful experiment by F. Reines and C. L. Cowan[6] in 1956, where the anti-neutrino source was the nuclear reactor at Savannah River in South Carolina [21].

Once the existence of electron neutrino was firmly established, the question still remained regarding its mass. The subsequent years, 1957–1958, were crucial in this respect. After the discovery of parity violation in the β-decay [22], the two-component theory put forward by T. D. Lee and C. N. Yang [23], L. D. Landau [24] and A. Salam [25] gave a strong indication of a massless neutrino, while the measurement of its helicity [26] identified the neutrino as a left-handed particle (the antineutrino being right-handed). But this perspective soon changed with the $V - A$ theory [27,28]: the Hamiltonian describing weak interactions involves the left-handed components of neutrino as well as other fermion fields, so there is no apparent connection between parity violation in weak interactions and peculiar properties of neutrinos. This conclusion led to questioning the idea of a massless neutrino, even if a few years later the Standard Model would have been constructed under this assumption. R. Davis [29] unsuccessfully attempted to detect antineutrinos via the electron capture reaction $\overline{\nu} + {}^{37}\mathrm{Cl} \to {}^{37}\mathrm{Ar} + e^-$ and showed that neutrino and antineutrino were different particles, barely contradicting Majorana's hypothesis [12]. Thus, a further question arose: what is the nature of massive neutrinos, Dirac or Majorana?

Indeed, Pontecorvo's idea of neutrino's oscillations [30,31], presented in 1957 and later generalized [32] in order to include the newly discovered *muon* neutrino ν_μ,[7] prompted the picture of massive neutrinos but, at the same time, was not able to discriminate between the Dirac and the Majorana nature of their mass, as the characteristic effects of Majorana neutrinos were suppressed in the ultra-relativistic regime (i.e., the regime of interest for neutrino's oscillations) due to the $V - A$ structure of weak interactions. Indeed he discussed a number of experiments [32] apt to test the conservation of lepton numbers and concluded that, besides nonzero neutrino masses, neutrino oscillations could take place only in the presence of a violation of lepton numbers induced by an additional interaction between neutrinos. In particular, he dealt with the oscillations of solar neutrinos and anticipated the *solar neutrino problem*. In a subsequent and comprehensive review [34], the concept of leptonic mixing [35–37] was fully exploited and the study of the phenomenon of neutrino oscillations was recognized as the most sensitive method to look for small neutrino mass squared differences. Then, growing evidence in favor of neutrino oscillations was obtained in a number of experiments involving neutrinos from natural sources, either atmospheric [38–40] or solar [41–47], as well as from reactors [48], while the DONUT experiment led to the discovery of the third neutrino flavor, ν_τ, in 2000 [49].

All the experiments on neutrino oscillations confirm the picture of neutrino flavor (ν_e, ν_μ, ν_τ) states as coherent superpositions of neutrino mass (ν_1, ν_2, ν_3) eigenstates[8] and point to tiny neutrino masses, much smaller than the masses of leptons and quarks, thus hinting at a new physics beyond the Standard Model. Furthermore, the interference nature of neutrino oscillations and the possibility to explore large values of the ratio $\frac{L_{sd}}{E}$, L_{sd} as the source–detector distance make the above experiments able to determine, besides neutrino mixing angles, very small values of the neutrino mass squared differences. On the other hand, they cannot provide an answer to the following fundamental questions: the determination of the absolute value of the neutrino masses and the investigation of the nature of the massive neutrinos (i.e., Majorana or Dirac particles). To this end new experimental strategies need to be devised and exploited, the ultimate challenge being to select, among various proposals of new theories beyond the Standard Model, the right one. Three main approaches have been put forward since Fermi [7–10] and Perrin [14] proposals based on the analysis of the β-decay spectrum:

- Direct method for neutrino mass determination.
  At the heart of direct neutrino mass determination, there is kinematics of weak decays of a number of isotopes, so the neutrino mass is obtained by means of the relativistic energy–momentum formula $E^2 = p^2 + m^2$. In principle, the method is sensitive to the neutrino mass squared m_ν^2 and dates back to Fermi's suggestion [7–10], independently pointed out by Perrin [14], of the investigation of the endpoint region of a β-decay spectrum or an electron capture. Usually the measurement of the charged decay products leads to the determination of the *average electron neutrino mass* as the incoherent sum over all the neutrino mass eigenstates m_i, $m_{\nu_e}^2 = \sum_i |U_{ei}^2| m_i^2$, where there is no contribution from the phases of the neutrino mixing matrix U_{ei}. The direct method is still the most sensitive one aimed to determine the absolute neutrino mass scale and it has the advantage of being model-independent.[9] Unfortunately, it cannot say anything about the nature of neutrinos.
- Neutrinoless double β-decay.
  The discovery of nonzero neutrino masses brought to the attention of scientists the fundamental and longstanding issue of the nature of neutrinos, and the related issue of the conservation of the lepton number L. In fact, if a neutrino is a Majorana fermion, the conservation of L is not an exact law of nature and its violation holds on [56]. Vice versa, the conservation of L is an exact law of nature for a Dirac fermion and $\Delta L = 2$, processes are strictly forbidden. The best experimental probe of lepton number conservation is, without any doubt, the neutrinoless double β-decay [57–60]. Here, the neutrino behaves as a virtual exchange particle and only two electrons are expected to be observed in the final state characterized by an energy sum close to the Q-value of the decay. Neutrinoless double β-decay is really a very rare and challenging process to observe and may occur only if the massive neutrino is a Majorana particle. In fact, the lifetime of the process is related to the effective Majorana neutrino mass $\langle m_{\nu_e} \rangle = \left| \sum_k m_k U_{ek}^2 e^{i\phi_k} \right|$. Here, the presence of the CP-violating Majorana phases ϕ_k could make the sum zero even in the presence of nonzero single neutrino masses. The process is also sensitive to the absolute scale of neutrino masses and to the mass hierarchy.
- Cosmology and astrophysics.

The actual structure of the universe is the result of fluctuations in the primordial universe. Relic neutrinos affect the distribution of matter in the universe, leaving a fingerprint on the cosmic microwave background, on the large-scale clustering of cosmological structure and finally on the primordial abundance of light elements. In fact, they smeared out fluctuations at small scales, whose order of magnitude could be found starting from the free streaming length of neutrinos, a function of their mass. Thus, information on the total neutrino mass $M_{TOT} = \sum_i m_i$, $i = 1, 2, 3$ can be gathered from satellite data as WMAP [61] and PLANCK [62], as well as from large galaxy surveys such as SDSS [63]. In this way, upper limits on the total neutrino mass have been obtained, the last one being $M_{TOT} < 0.11$ eV at 95% confidence level, albeit model- and analysis-dependent.

Information about neutrino mass can be gathered also using neutrinos from very strong sources, such as astrophysical events like a core-collapse supernova. Very long baselines are also required in order to carry out time-of-flight measurements. The supernova explosion SN1987A in the Large Magellanic Cloud, which has been the only one detected via neutrinos, provided the following limits on the electron antineutrino mass, $m_{\overline{\nu}_e} < 5.7$ eV [64] and $m_{\overline{\nu}_e} < 5.8$ eV [65], at 95% confidence level, depending on the underlying supernova model as well as on the chosen data analysis techniques. Currently, nearby supernova explosions are extremely rare and the underlying mechanism still lacks a complete understanding. These considerations make direct laboratory neutrino-mass experiments the best experimental choice to obtain a determination of the neutrino mass.

Neutrino physics has been the subject of a number of historical studies, mainly covering general aspects [66–68] or focusing on particular issues such as the oscillations and mixing phenomena [69–72], but a comprehensive historical account of the underlying theoretical principles and the huge experimental efforts carried out to determine the absolute neutrino mass scale and its nature as Dirac or Majorana particle is still lacking. The aim of this work is to fill this gap. In particular, we focus on the methods and techniques devoted to the direct measurement of the absolute electron neutrino (antineutrino) mass scale, starting from the first proposals [7–10,14] and ending with the most recent developments. The history of the neutrinoless double β-decay is retraced as well as a tool to address the issue of the nature of neutrino.

The paper is organized as follows.

In Section 2, direct measurements of the electron neutrino (antineutrino) rest mass are presented starting from the first investigations of the β-decay spectrum and going through orbital electron capture experiments. Then, the attention is focused on tritium, and finally, a brief account of recent experiments and techniques is given.

In Section 3, the neutrinoless double β-decay phenomenon is historically retraced, focusing mainly on the issue of the nature of neutrinos as Dirac or Majorana particles and on the related experimental attempts to probe them. The related process of resonant neutrinoless double electron capture is also briefly discussed.

Finally, our concluding remarks are given in Section 4.

2. Direct Neutrino Mass Determination

In this section, we retrace the history of experimental efforts and techniques devoted to the direct determination of the absolute mass scale of neutrinos. The focus is on the electron neutrino (and antineutrino).

Direct methods do not require the non-conservation of the total lepton number (or family lepton number) and are essentially based on the kinematics of β-decays of a number of isotopes (for instance ^{3}H and ^{187}Re). In principle, by measuring the momentum of charged decay products and using the energy–momentum conservation, the mass of the outgoing neutrino can be determined. In this way, model-independent information is obtained, but a critical point of the method is the smallness of the neutrino mass, which requires a careful control of the experimental errors. Only upper limits for the neutrino masses can be extracted. With reference to the electron neutrino ν_e (or antineutrino), the most sensitive method since Fermi's pioneering work [7–10] is the investigation of the shape of the *endpoint* of the β-decay spectrum, i.e., its high-energy part, which is dependent on the neutrino mass as $E_e^{max} \simeq Q - m_{\nu_e}$. Since the first estimate carried out in 1947 by E. J. Konopinski [73], the use of tritium as the standard isotope in these experiments has been growing up because of a low Q-value (18.6 keV), a rather short half-life (12.3 yr), a low nuclear mass and a simple shell structure [50]. An experimental setup, besides the source, consists of a magnetic transport system, a spectrometer and a detector. Various technological advances related to the spectrometers have been introduced as well in tritium experiments since the 1990s to improve sensitivity, such as, for instance, the MAC-E filter technology fully exploited within the KATRIN experiment [74].

Possible experimental probes for the determination of neutrino masses also include charged lepton decays, meson decays and electron and neutrino capture processes in nuclei. Isotopes of interest, other than tritium, are mainly ^{187}Re and ^{163}Ho [55]. Experiments based on ^{187}Re exploit a first-order forbidden β-decay process, which makes the observation of decay events near the endpoint of rhenium very challenging and requires microcalorimetric techniques in order to carry out accurate measurements. Calorimetric techniques are the basis also of neutrino mass experiments involving ^{163}Ho, but here, an electron capture decay process is exploited.

2.1. The β-Decay Spectrum and Early Experiments

In the late 1920s the existing picture of the β-decay was that of a process characterized by a primary nucleus (A, Z) decaying into a secondary one with a different (by one unit) charge and an electron (or a positron), namely $(A, Z) \to (A, Z \pm 1) + e^{\mp}$. In this situation, without additional particles in the final state, the energy content of $e^{\mp}$ should be given by a single value $E_e \simeq Q = M_{A,Z} - M_{A,Z\pm1}$, at odds with the known experimental results, pointing to a continuum spectrum of allowed energies up to a maximum endpoint value Q. Among the first explanations of this puzzling behavior is the degradation in energy of the β-particle in passing through the target. Subsequent experiments by C. D. Ellis and W. A. Wooster [75] showed that the average energy associated with the β-disintegration of Radium E was 0.35 MeV, in full agreement with the average energy value extracted from the observed continuous β-spectrum and, in particular, lower than the total energy released in the process. As such, either the validity of the energy–momentum principle had to be questioned within nuclei (as envisaged by N. Bohr [4]) or some of the energy released in the process was carried out by new radiation, still undetectable with the available techniques. The second option was advocated by W. Pauli [1,2], who postulated the existence of a neutral particle with a mass smaller than that of the electron, spin $\frac{1}{2}$, and a penetrating power greater than that of photons with the same energy, in order to guarantee the energy–momentum conservation.

Pauli's suggestion fostered subsequent proposals aimed at fully explaining the β-decay spectrum, which culminated in the celebrated Fermi's theory [7–10]. At the heart of his model is a very short-range interaction between two weak currents, the first one involving the initial and final state of the nucleus and the second one the electron and the new neutral particle (i.e., the anti-neutrino) appearing in the final state. In particular, the sum of the kinetic energies of the β-particle and the associated neutrino equals the maximum kinetic energy of the β-spectrum while the discrete structure of nuclear energy levels is kept. Furthermore, the very large nuclear mass with respect to electron and neutrino masses makes the kinetic energy of the recoil nucleus negligible within the energy balance.

Starting from a second-quantized Hamiltonian for the system of heavy and light particles in interaction and using the time-dependent perturbation theory, Fermi calculated the transition probability per unit time of a β-decay with emission of an electron in the state s as [7–10]:

$$P_s = \frac{8\pi^2 g^2}{h^4} \left| \int v_m^* u_n d\tau \right|^2 \frac{p_\sigma^2}{v_\sigma} \left(\tilde{\psi}_s \psi_s - \frac{\mu c^2}{K_\sigma} \tilde{\psi}_s \beta \psi_s \right), \tag{1}$$

where g is the coupling constant, v_m and u_n are the eigenfunctions of the proton and the neutron, respectively, ψ_s is the normalized eigenfunction of the electron in the state s, v_σ, p_σ and K_σ are the velocity, the momentum and the energy of the neutrino in the state σ, μ is its rest mass[10] and β is the Dirac matrix. Fermi pointed out the analogy between the matrix element $Q^*_{mn} = \int v^*_m u_n d\tau$ of Equation (1), involving the eigenfunctions of heavy particles, and the matrix element of the electric moments of an atom in radiation theory and hinted to the possibility of forbidden transitions when $Q^*_{mn} = 0$.[11] Then, he derived the following conditions to be fulfilled for the occurrence of β-decay: (a) $H_s \leq W - \mu c^2$, where W is the energy difference between the neutron and the proton states, H_s is the energy of the electron in the state s and the equality gives the upper limit of the spectrum; (b) $W \geq (m_e + \mu)c^2$, because a free electron state is such that $H_s > m_e c^2$. Finally, Equation (1) allowed Fermi to derive the shape of the continuous β-spectrum. He found a remarkable dependence on the rest mass μ of the neutrino near the endpoint of the curve and was able to determine its value by comparison with empirical curves. In particular, denoting by E_0 the maximum energy of the β-rays, the qualitative behavior of the curve for energy values E near E_0 was given by:

$$\frac{p_\sigma^2}{v_\sigma} = c^{-3}\left(\mu c^2 + E_0 - E\right)\left[(E_0 - E)^2 + 2\mu c^2 (E_0 - E)\right]^{1/2}, \tag{2}$$

and drawn for $\mu = 0$ as well as for small and large values of μ, respectively, as in Figure 1 (see Ref. [10], p. 1156).

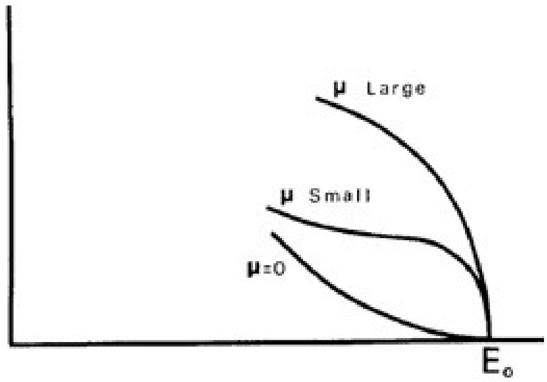

Figure 1. Qualitative behavior of the β-ray spectrum near the endpoint for various values of μ (reprinted with permission from Ref. [10]. 2024, AIP Publishing).

Interestingly his conclusions were as follows:

> The greatest similarity to the empirical curves is given by the theoretical curve for $\mu = 0$. Hence, we conclude that the rest mass of the neutrino is either zero or, in any case, very small in comparison to the mass of the electrons ([10], p. 1156).

He also added a footnote, pointing out that analogous conclusions had been drawn by F. Perrin in a recent publication [14]. Then, in the simplest case of a neutrino with zero rest mass, from Equation (1) (where $\mu = 0$ was taken), he obtained the simplified expression:

$$P_s = \frac{8\pi^2 g^2}{c^3 h^4}\left|\int v^*_m u_n d\tau\right|^2 \tilde{\psi}_s \psi_s (W - H_s), \tag{3}$$

Finally, from Equation (3), after lengthy calculations (taking the values $R_{nucleus} = 9 \times 10^{-13}$ for the nuclear radius and $Z = 82.2$ for the atomic number, which is indeed very close to the atomic numbers of the radioactive elements), he derived a formula for the inverse lifetime of allowed transitions [7–10]:

$$\tau^{-1} = 1.75\left(10^{95}\right)g^2\left|\int v_m^* u_n d\tau\right|^2 F(\eta_0), \tag{4}$$

where η_0 is the maximum momentum of the β-particles measured in units of mc and $F(\eta_0)$ is the following:

$$F(\eta_0) = \frac{2}{3}\left[\left(1+\eta_0^2\right)^{\frac{1}{2}} - 1\right] + \frac{1}{12}\eta_0^4 - \frac{1}{3}\eta_0^2 + 0.355\left\{ -\frac{1}{4}\eta_0 - \frac{1}{12}\eta_0^3 + \frac{1}{30}\eta_0^5 + \frac{1}{4}\left[\left(1+\eta_0^2\right)^{\frac{1}{2}}\right] log\left[\eta_0 + \left(1+\eta_0^2\right)^{\frac{1}{2}}\right]\right\}. \tag{5}$$

Equation (4) established a link between the maximum momentum of the β-particles η_0 and the lifetime of the decaying substance and allowed Fermi to make a comparison with experiments. For all allowed transitions the order of magnitude of the matrix element $\int v_m^* u_n d\tau$ was $\simeq 1$, leading to the same order of magnitude for the product $\tau F(\eta_0)$, while in the case of a forbidden transition a lifetime about 100 times greater resulted, giving rise to a larger value of $\tau F(\eta_0)$. Fermi computed this product for nine radioactive elements, whose experimental data on continuous spectra were available, and found a good agreement with the above theoretical predictions. In fact, the first group of five elements was identified with a $\tau F(\eta_0)$ value within a range $1 \div 3$, while for the remaining four elements values from 190 to 1800 were obtained [7–10]. Subsequent extensive calculations of $\tau F(\eta_0)$ values for a wide number of radioactive β-transitions confirmed Fermi's results and, in particular, his empirical classification of allowed and forbidden transitions [76].

Fermi's conclusions on β-spectrum were remarkable [77]. His theory allowed him to predict a new process, the capture of an orbital electron by a nucleus, and made β-spectroscopy a valuable tool for investigating the structure of nuclei. It was G. C. Wick who, in 1934, showed that Fermi's theory also described in a natural way the emission of positrons according to the process ${}^1_1p \rightarrow {}^1_0n + e^+ + \nu$ and went on predicting the possibility of K-electron capture in radioactive nuclei [78], ${}^1_1p + e^- \rightarrow {}^1_0n + \nu$, which would have been experimentally found later by L. W. Alvarez [79,80].[12] But some disagreement between Fermi's theoretical expressions and experimental β-spectra was soon pointed out [81], demanding a modification of his theory. Starting from a thorough analysis of Fermi's assumptions [7–10], E. J. Konopinski and G. E. Uhlenbeck [82] put forward a modified interaction Hamiltonian, where the neutrino wave function was replaced by the corresponding first derivative. Their proposal was effective in changing the transition probability by the introduction of a weight factor able to shift the distribution towards low electron energies or high neutrino energies. The output was a close agreement with experimental data, further confirmed within a series of measurements carried out by F. N. D. Kurie, J. R. Richardson and H. C. Paxton [83]. They gave a seminal contribution to the studies of continuous β-spectra by introducing a new method of analysis of the shapes of such spectra, the Fermi–Kurie (F-K) plot, which is much more suitable to identify the effect of the neutrino mass. The procedure runs as follows: starting from the experimental values of the number of electrons emitted per unit time as a function of the momentum p_e within the momentum interval Δp_e, $\frac{dN}{dp_e}\Delta p_e$, the quantity

$$\left[\frac{dN}{dp_e}\frac{1}{p_e^2}\frac{1}{F(Z,p_e)}\right]^{1/2}, \tag{6}$$

has to be calculated and plotted against $E_0 - E$. Here, E_0 is the upper limit energy and $F(Z,p_e)$ is the Fermi function, which takes into account the influence of the nuclear charge on the wave function of the emitted electron. Indeed, the F-K plot amounts to a linearization of the β-spectrum if Fermi's theory is fulfilled and the rest mass μ of the neutrino is zero, with E_0 being the intercept on the E-axis. When dealing with the Konopinski and Uhlenbeck [82] modification, the F-K distribution becomes:

$$\left[\frac{dN}{dp_e}\frac{1}{p_e^2}\frac{1}{F(Z,p_e)}\right]^{1/4} = const \cdot (E_0 - E), \tag{7}$$

and a straight line signals the agreement of experimental data with Konopinski and Uhlenbeck's theory.

But in general, the experiments carried out in the mid-thirties were not able to provide accurate results for the upper limits of β-spectra due to the scattering of the β-particles, which made range measurements quite indefinite. As a consequence no simple relation to the maximum energy of the β-particles could be established and new techniques of data analysis were needed. Measurements carried out by W. J. Henderson [84] with a coincidence counter method led to accurate values for the upper energy limits of thorium C and thorium C'', which were indeed equal as predicted by C. D. Ellis and N. F. Mott [85]. Furthermore, an investigation of the emission of β-electrons (${}^{12}_{5}\mathrm{B} \rightarrow {}^{12}\mathrm{C} + e^- + \overline{\nu}$) with very high energy from boron bombarded with deuterons (${}^{11}_{5}\mathrm{B} + {}^{1}_{2}\mathrm{D} \rightarrow {}^{12}_{5}\mathrm{B} + {}^{1}_{1}\mathrm{H}$) was performed as well, by means of a cloud chamber [86]. The electron tracks were curved by a 1500 Gauss magnetic field in order to measure their energy, giving an upper energy limit $E_0 = 11$ MeV. Finally, the energy balance was tested by considering also the process ${}^{11}_{5}\mathrm{B} + {}^{1}_{2}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}n$, whose energy release was about 13 MeV. A comparison with the previous process allowed us to establish the following relation

$$m\left({}^{12}B\right) \geq m\left({}^{12}C\right) + 11\ MeV. \tag{8}$$

The resulting energy difference, 2 MeV, led to the conclusion that boron, upon disintegration, loses a mass quantity not less than that corresponding to the upper energy limit of the β-spectrum [86], providing further confirmation of neutrino hypothesis.

The correlation between the shape of the β-spectrum near the endpoint energy of the electrons and the mass of the neutrino was further discussed in 1936 by Bethe and R. F. Bacher [87] and later by O. Kofoed-Hansen [88], while both Bethe [89] and Crane [16] pointed out how to make an estimate of the mass of the neutrino by means of a closed cycle, built of a p-n reaction followed by positron emission. A couple of interesting examples were also discussed [16,90]. The first one deals with a measurement of the energy threshold of the closed cycles ${}^{13}\mathrm{C} + p \rightarrow {}^{13}\mathrm{N} + n$, ${}^{13}\mathrm{N} \rightarrow {}^{13}\mathrm{C} + e^+ + \nu$ and ${}^{11}\mathrm{B} + p \rightarrow {}^{11}\mathrm{C} + n$, ${}^{11}\mathrm{C} \rightarrow {}^{11}\mathrm{B} + e^+ + \nu$, both involving a neutrino [91]. Concerning the first cycle, the value obtained for the energy available for the ${}^{13}\mathrm{N}$ decay was (1.20 ± 0.04) MeV, to be compared with the endpoint energy of the ${}^{13}\mathrm{N}$ spectrum obtained within an analogous experiment [92], (1.198 ± 0.006) MeV. As a result, the energy equivalent of the mass of the neutrino obtained, (0.0 ± 0.07) MeV, was very small. Likewise for the second cycle, which gave an energy equivalent of the mass of the neutrino of (0.001 ± 0.0056) MeV. The second example refers to a measurement of the energy release within the cycles ${}^{14}\mathrm{N}\ (n,p)\ {}^{14}\mathrm{C}$, ${}^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + e^- + \nu$ and ${}^{3}\mathrm{He}\ (n,p)\ {}^{3}\mathrm{H}$, ${}^{3}\mathrm{H} \rightarrow {}^{3}\mathrm{He} + e^- + \nu$ [93]. The estimate of the mass of the neutrino, obtained by substituting in the closed cycle the neutron-proton mass difference and the mass of the electron (and including the energy available for the ${}^{14}\mathrm{C}$ and the ${}^{3}\mathrm{H}$ decay, respectively, in the first and second reaction), gave the values (1 ± 25) keV and (4 ± 25) keV for the first and the second cycle under study, i.e., a value within 5 keV in both cases. However, as pointed out in Refs. [16,54], the uncertainty on the measurement of the total energy release in β-decay affected the accuracy of the value of the neutrino mass determined by means of closed cycle reactions, requiring further improvements. Further measurements of the upper limit of the β-ray spectrum from ${}^{3}\mathrm{H}$ were carried out by R. J. Watts and D. Williams in 1946 [94]. A novel method was employed, based on a Geiger counter equipped with a thin window, whose effective thickness was evaluated by the acceleration of electrons produced by a hot filament. Then, accelerating potentials were applied between the source (built on an electrode) and the window of the counter until the β-particles were able to pass through the window. Finally, these two measurements allowed us to determine the upper limit of the spectrum giving the result (11 ± 2) keV.

An interesting study of β-radiation from ^{64}Cu, i.e., in the case of a (super)-allowed Fermi transition, was carried out in 1939 [95] in order to investigate the effect on the shape of the β-spectrum of the scattering within the source. As such, sources of different thicknesses were employed ranging from thicker to extremely thin ones. The net result was a spectrum containing fewer low-energy particles in correspondence to thinner sources and showing a better agreement with Fermi's theory [7–10], whereas the modifications introduced by a thicker source would eventually be compatible with the Konopinski and Uhlenbeck theory [82]. Furthermore, the departure from Fermi's distribution still present in the low-energy region of the β-spectrum had to be ascribed to an excess of electrons therein, probably hinting to a possible failure of Fermi's theory in taking into account the effect of the nuclear charge [95]. This issue would have been the subject of further investigation at the end of the 1940s, mainly focused on the β-radiation produced by ^{35}S [96] and ^{64}Cu [97,98] sources and aimed at evaluating the effect of the Coulomb correction on the low-energy region of the corresponding spectra. In the first case, a linear F-K plot over the whole range of the spectrum was obtained by using sources with an average thickness close to one microgram per square centimeter [96], while in the second case, small deviations of F-K plots from straight lines were still observed in the low-energy region, albeit gradually decreasing as a function of the source thickness. The effect of more uniform sources as well as of an improved Coulomb correction factor was addressed as well, leading to a residual deviation of F-K plots probably due to instrumental uncertainties [97,98]. The β-spectra of ^{14}C and ^{35}S were investigated also by C. S. Cook, L. M. Langer and H. C. Price [99] by means of a large magnetic spectrometer. For ^{35}S, an allowed transition took place and an agreement between the observed and the theoretical spectrum was obtained within the energy region from 1.15 $m_e c^2$ to the endpoint $E_0 = 1.331\ m_e c^2$, while the lower energy portion of the spectrum showing deviations from Fermi's theory. The F-K plot within the same energy range was a straight line, with the endpoint value corresponding to a kinetic energy of (169.1 ± 0.5) keV. If compared with the ^{3}H endpoint energy, about 18 keV, the ^{35}S higher value would result less amenable to a determination of neutrino mass. In fact, Cook, Langer and Price's conclusion was as follows:

> The experimental points [...] are consistent with a neutrino rest mass of zero. Within the limits of error one can certainly say that the mass of the neutrino is less than one percent the mass of the electron ([99], p. 552).

This clearly means an upper limit of about 5 keV for the mass of the neutrino. Concerning the ^{14}C disintegration, the extremely long half-life (about 5100 yr) put it within forbidden transitions and the observed spectra showed a behavior not consistent with the predictions of Fermi selection rules [99].

Among the possible experimental methods for the detection of neutrinos, there is the observation of the recoil of the nucleus within a radioactive decay characterized by the emission of a neutrino. Here, the measurement of the momenta of both the nucleus and the electron and the angle between them is needed in order to determine the momentum and the mass of the neutrino. The first (and simplest) instance of recoil experiments, based on β-decay theories, modeled the escape of the missing energy via a single package (the neutrino), while further improvements led to a picture of the nucleus losing its excess energy via multiple packages [16]. The first attempt to observe the recoil of the nucleus and then measure its momentum was carried out by A. I. Leipunski in 1936 [100]. He had to overcome major experimental difficulties related to the order of magnitude (1 eV) of the energy of recoil atoms of ordinary radioactive substances, very small and comparable with that of the adsorption energy of the atoms on a surface. The solution was to choose an artificial radioactive substance, the carbon $^{11}_{6}$C, obtained by bombarding boron with deuterons. He tried to measure the distribution of $^{11}_{5}$B nuclei produced via the β-decay $^{11}_{6}\text{C} \rightarrow\ ^{11}_{5}\text{B} + e^+ + \nu$. The radiocarbon, in the form of carbon dioxide and monoxide, was condensed on a surface cooled by liquid air. A retarding electric field was applied between the cold surface and a grid, allowing only a fraction of recoil nuclei to pass the grid, i.e., only the nuclei with energy greater than a fixed value. On the other side of the grid, the recoil nuclei were accelerated by a 5000 V potential towards a surface characterized by a low work function and detected through the secondary electrons emitted by the same surface. Despite the many critical points, essentially due to the uncertainty related to the escape of $^{11}_{5}B$ recoil nuclei from the surface, Leipunski's experiment was the first successful attempt to detect recoil nuclei and paved the way to further experiments based on momentum relations in β-decay processes, as vividly observed by Crane [16]:

> It seems to be futile to try to apply the corrections which would be necessary for the interpretation of the Leipunski experiment. Nevertheless the experiment had great value in that a successful method of detecting recoil nuclei was found for the first time, and the way was thereby opened for a succession of experiments on the momentum relations in the beta-decay ([16], p. 285).

Further experiments aimed at detecting the neutrino through the simultaneous measurement of the recoil of nuclei as well as electrons were carried out by Crane and J. Halpern [101,102], with reference to the disintegration of the radiochlorine according to the process $^{38}Cl \rightarrow\ ^{38}Ar + e^- + \bar{\nu}$. The radioactive ^{38}Cl in the form of gaseous ethylene dichloride was introduced in a cloud chamber, and then the momentum of the emitted electrons was measured through the curvature of their tracks in a magnetic field. The momenta of recoil nuclei were determined with poor accuracy due to the lack of a quantitative relation between the number of droplets produced by these nuclei in the cloud chamber and their kinetic energy content. Despite the above drawbacks, the main conclusion was the momentum non-conservation in the system consisting of the electron and nucleus alone, in agreement with the neutrino hypothesis. In principle, the angular distribution between electron and neutrino could have been extracted as well from experimental data, but significant experimental uncertainties prevented this option [101,102].

The correlation between the directions of emission of the electron and the neutrino within β-decay had been first investigated by F. Bloch and C. Moller in 1935 [103]. They recognized that, when dealing with the recoil of a light nucleus, the angular distribution of the neutrino is not isotropic for a given direction of the electron. In particular, for an allowed Fermi transition, the relative probability of decay with an angle θ between electron and neutrino directions was predicted to be given by the correlation function $P(\theta) = 1 + \frac{v}{c} cos\theta$, where v and c are the velocities of the electron and of the light, respectively. These calculations were later generalized by D. R. Hamilton [104] to the allowed as well as the first forbidden transitions corresponding to the five Lorentz invariant forms of β-interactions. The resulting correlation functions were very different for the different possible interactions and, in the case of forbidden transitions, a progressive enhancement of the emission of the neutrino along the direction of the electron took place upon increasing the order of transitions. The above findings were soon experimentally tested by C. W. Sherwin [105,106] by using highly concentrated sources made of thin layers deposited on a suitable backing. He investigated the recoil spectra from thin sources of ^{32}P and ^{90}Y by recording the β-particles with an end-window Geiger counter and the recoil nuclei with an electron multiplier tube. The velocity distribution of the nuclear recoils was measured by a time-of-flight technique in both cases. As a result, for the ^{32}P source the observed recoil momentum spectra taken at 180° were compatible with the neutrino hypothesis and with the correlation function $1 - \frac{v}{c} cos\theta$, while the curve at 135° was better fitted by the correlation function $\left[1 - \frac{v}{c} cos\theta\right]^2$ [105]. On the other hand, for the ^{90}Y source, the neutrino hypothesis was confirmed as well, but a discrepancy was found between observed and calculated spectra, both at 180° and at 135°, probably due to surface effects on the chemical bonds [106].

The above discussion of early experiments on β-decay shows how the final region of the spectrum, near the upper energy limit, is crucial for the experimental determination of the rest mass of the neutrino. While Fermi's proposal relies on the comparison between experimental and theoretical spectra to infer that the mass of the neutrino is smaller than the electron mass (about $\frac{1}{5}$), a simpler estimate has been proposed later in terms of the maximum β-energy E_0 (which contains the electron rest mass $m_e c^2$) and of the mass differences between the primary and the secondary nucleus [91,92]:

$$\Delta M c^2 = E_0 + \mu c^2, \tag{9}$$

μ being the mass of the neutrino.

In this respect, a strict relation between the shape of the β-spectrum in the proximity of the endpoint energy and the rest mass of the neutrino was put forward by Kofoed-Hansen [88] in 1947. His starting point was the consideration that a neutrino mass smaller than that of the electron could affect only the shape of the spectrum near the endpoint, where on the other hand, the probability of the emission of a β-particle is small. As a consequence, in the case of a nonzero neutrino mass, the endpoint energy had to be evaluated by extrapolation as $E_{ex} = E_0 + \mu c^2$. The result was an F-K plot showing small deviations from the straight line pattern only in the narrow energy range $(\Delta M - 2\mu)c^2 < E < \Delta M c^2$ near the upper limit. In his words:

> The thesis that the maximum β-energy can only be determined with the same accuracy as can the mass of the neutrino, has here been illustrated in the special case of the Fermi theory, which fits experimental data rather closely, but it is not restricted to this theory alone ([88], p. 452).

In principle, according to the above conclusions, an upper limit for the neutrino mass could be extracted when considering processes characterized by a negligible E_0 value, for instance ^{3}H $\to$ ^{3}He, but the lack of sufficient accuracy in the mass difference between the two nuclei put severe drawbacks on this possibility.[13] A better estimate of the mass of the neutrino could be obtained by investigating the endpoint region of the β-spectra with improved experimental setups and techniques. These improvements and the corresponding estimates of the neutrino mass will be the subject of the following subsections.

2.2. The β-Spectrum of ^{3}H: Early Experiments

Today, the main efforts towards the direct determination of the neutrino mass are focused on tritium, the heaviest hydrogen isotope, which undergoes a super-allowed β-decay, $^3\text{H} \to {}^3\text{He}^+ + e^- + \overline{\nu}$, characterized by a half-life 12.3 yr [50,53]. Tritium has a nuclear matrix element close to that of β-decay of the free neutron and equal to $\left|\int v_m^* u_n d\tau\right|^2 \simeq 5.55$ and an endpoint energy $E_0 = 18.6$ keV. All these features together with a simple electronic structure make its β-spectrum the best choice for a measurement with small systematic uncertainties. The aim of this subsection is to retrace the history of direct neutrino mass measurements based on tritium since the first estimate carried out by Konopinski in 1947 [73].

The starting point of Konopinski's work [73] is the analysis of earlier tritium endpoint measurements carried out by Watts and Williams in 1946 [94]. Indeed, the very low value obtained for the maximum energy, (11 ± 2) keV, led to a calculated lifetime extremely sensitive to the rest mass of the neutrino. So, he found that only a neutrino mass within the range from $\frac{1}{30}$ to $\frac{1}{45}$ of the electron mass m_e (i.e., within the range $11 \div 17$ keV) should be compatible with an agreement between the calculated and the measured lifetime, while a massless neutrino should lead to a discrepancy of a factor 10. Further estimates based on the relation between half-life and energy release in β-decay of ^{3}H were provided by J. R. Pruett [108], who considered the very short half-life of ^{3}H (about $10 \div 20$ yr) corresponding to an energy release within the range $11 \div 15$ keV. In particular, for a half-life of 20 yr an energy release of 11 keV gave a neutrino rest mass of 0.277 m_e, while the smaller value 0.054 m_e was found in correspondence to the higher energy release 15 keV. Finally, an energy release equal to or higher than 20 keV would produce a zero mass for neutrino.

The first measurements of the shape of the ^{3}H β-spectrum were carried out in 1948–1949 by S. C. Curran, J. Angus and A. L. Cockroft [109,110] by using novel proportional counter methods, ad hoc designed to address the drawbacks connected to the analysis of spectra near the low-energy end. The radioactive element was fed directly into the proportional counter as a gaseous constituent, and then the output pulses were applied to the deflecting plates of a cathode ray tube and recorded by a moving-film camera [109]. The size of these pulses gave a measure of the energy of the ionizing particles involved so that from their histogram, the shape of the spectrum was obtained. This technique was shown to be effective in limiting the absorption of electrons within finite thickness sources and supports usually employed in β-spectroscopy experiments. On the other hand, the accuracy of the energy measurements would be reduced due to the finite energy resolution of the counter and to end effects. In these experimental conditions, the finite resolving power of the tube did not significantly affect in general the shape of the β-distribution, which was in good agreement with Fermi's theory. Some effects were found only within a region of about 1 keV near the endpoint E_0, whose estimate was (17.9 ± 0.3) keV [110], the best agreement with the theoretical predictions being at a neutrino rest mass value of $\frac{m_e}{500} \simeq 1$ keV ($m_e = 0.511$ MeV is the electron rest mass) as shown in Figure 2 (see Ref. [110], p. 60).

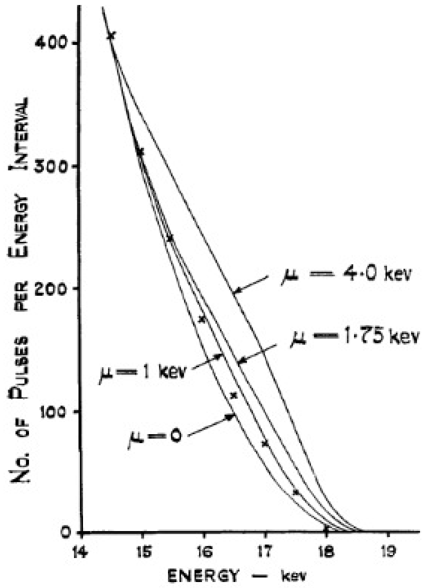

Figure 2. Theoretical curves corresponding to various values of neutrino rest mass μ of 0, $m_e/500$, $m_e/300$, $m_e/125$. Crosses indicate experimental values (reprinted with permission from Ref. [110]. 2024, Taylor & Francis).

Further improvements in the energy resolution led to better accuracy in the determination of the spectrum near the endpoint energy [111]. The theoretical curves were calculated for true endpoints $E_0 = 18.0$ keV and $E_0 = 18.6$ keV and a neutrino rest mass $\mu = 0$ keV, then for $E_0 = 18.0$ keV and a neutrino rest mass $\mu = 1$ keV, and compared with experimental points. In the case $\mu = 0$, the points were found to lie between the two theoretical curves for $E_0 = 18.0$ keV and $E_0 = 18.6$ keV, in close agreement with G. C. Hanna and Pontecorvo results [112,113], obtained with two proportional counters and compatible with a neutrino rest mass μ within the range $0 \div 1$ keV.

A direct investigation of the ^{3}H spectrum was carried out in 1952 by L. M. Langer and R. J. D. Moffat with a high-resolution magnetic spectrometer [114]. A huge effort was devoted to developing source preparation and detection techniques in order to overcome current drawbacks in spectrometer measurements and to obtain a high-quality β-distribution for ^{3}H. To this end, the spectrometer was operated at 0.7 percent momentum resolution, so that a correction would needed only for points recorded within 2 percent of the maximum energy.[14] The key point was the smallness of the required correction if compared with the effects under study. Furthermore, in order to meet the requests of a thin and uniform source,[15] the tritiated succinic acid was employed due to its stability at room temperature and its specific activity of 0.9 mc/μg. The grounding of the source was a key issue as well in order to prevent electrostatic charging. Finally, the choice of the detector had to guarantee a sensitivity independent of the electron energy over a large part of the distribution as such a G-M counter was used. The experimental data were consistent with a straight line F-K plot within the range from 5.5 keV to the endpoint energy (17.95 ± 0.10) keV, giving an upper limit of 250 eV (or equivalently 0.05 percent of the mass of the electron m_e) for the rest mass μ of the neutrino.[16] A new estimate of the comparative half-life of the super allowed transition $^3\text{H} \rightarrow\ ^3\text{He}$ was also provided, (1014 ± 20) s.

Further work on the shape of the tritium β-spectrum near the endpoint was carried out by D. R. Hamilton, W. P. Alford and L. Gross [117] by means of a spherical electrostatic integral spectrograph [118]. The aim was to investigate the possible effects of a nonzero neutrino mass. Due to the low endpoint energy of about 18 keV, source effects were a serious drawback that could be circumvented by focusing mainly on the last portion (a region of a few kilovolts) of the spectrum. Under these conditions, the effect of the source thickness was simply to convert the differential spectrum to an integral spectrum near the endpoint. The source was essentially made of tritium absorbed in a layer of 100 μg/cm^2 of zirconium deposited on a tungsten button [119], while the spectrograph acted as an integrating device. So, the outgoing electrons (from a source at the center of the sphere) passed through a retarding field, and only those with an energy higher than a fixed value reached the collector [118]. As a result, the collector current in correspondence of a given retarding voltage was the double integral of the β-spectrum. The assumption of a quadratic behavior for the continuous differential β-spectrum near the endpoint (for zero neutrino mass) led to a collector current proportional to the fourth power of the retarding voltage, $J(E) \sim (E_0 - E)^4$. Accordingly, an upper limit to the neutrino mass was found, equal to 500 eV, 250 eV and 150 eV, respectively, for the Dirac, Majorana and Fermi forms of the β-interaction, in good agreement with previous findings referring to the ^{35}S spectrum [99]. Finally, an estimate of the zero mass neutrino endpoint value was provided as (17.6 ± 0.4) keV.

Two interesting experiments based on high-resolution spectrometers were carried out in 1969. The first one by R. C. Salgo and H. H. Staub [120] made use of an electric retarding potential spectrometer in order to overcome the drawbacks set by finite resolution and source thickness effects. A strong T_2O source, spread over a wide area, was taken and a plane arrangement of the experimental apparatus was chosen. Then, an upper limit (within 80% confidence) of 200 eV for the rest mass of the antineutrino was obtained, independently of the structure of the source and the resolving power of the spectrometer. For a zero antineutrino rest mass, an estimate of the upper energy limit of the β-particles of (18.72 ± 0.05) keV was provided, with a corresponding ft value given by (1159 ± 11) s. The second experiment by R. Daris and C. St-Pierre [121] addressed the critical issues of Langer and Moffat work [114], in particular the effects on the β-spectrum due to the finite resolution of the instrument as well as to the accumulation of charge on the source. The main features were the use of a magnetic spectrometer with a momentum resolution of 0.25% and of a source characterized by a high specific activity, made by absorption of tritium into aluminum foil in a gaseous discharge. The resulting endpoint energy of the β-spectrum was (18.570 ± 0.075) keV, which gave a ft value of (1130 ± 15) s. Then, from the analysis of the upper 1 keV part of the measured spectra, an upper limit of 75 eV on the neutrino rest mass was extracted.

Further experimental investigations of the endpoint region of the β-spectrum for tritium were carried out in 1972 by K. E. Bergkvist [122,123]. The combined electrostatic-magnetic β-spectroscopic methods employed allowed him to achieve an improvement of about three orders of magnitude with respect to the usual intensity conditions of more conventional β-spectroscopic techniques. By paying attention also to the production of a high-quality source and to better control of the background, Bergkvist was able to perform a study of the tritium spectrum much closer to the endpoint than previous investigations.

Under these conditions, upper limits of 55–60 eV on the electron neutrino mass and on the Fermi energy of a universal neutrino or antineutrino degeneracy were obtained [122]. Finally an endpoint energy value of (18.610 ± 0.016) keV was established, with an inferred ft equal to (1148 ± 3) s [123]. In spite of his significantly improved upper limits on neutrino rest mass, Bergkvist's conclusion was that further refinements could have been obtained only including the effects of the distribution of atomic or molecular final states [124], i.e., solving the *final state problem*.

Another magnetic spectrometer experiment was performed by B. Röde and H. Daniel [125], who for the first time demonstrated the key role of a detailed treatment of energy losses in the source material. They found that a finite source thickness could mask the effect of a finite neutrino mass. The source was a thin film (with a thickness between 4 and 6 $\mu g/cm^2$) fabricated by spreading out a solution of tritiated polystyrene in benzene on water. An extrapolated endpoint energy value of (18.649 ± 0.074) keV was found, and, then, an upper limit of 86 eV (at 90% confidence) was established.

The experiments above described testify to the key role of magnetic spectrometers in obtaining the lowest upper limits for the antineutrino (neutrino) rest mass. Such spectrometers were effective in measuring the momentum distribution of β-particles over a small region close to the endpoint and obtained a good resolution, close to $\sim$50 eV. Unfortunately, they showed a number of drawbacks related mainly to the geometry and thickness of the high-activity source needed and to the background effects from multiple scattering. As pointed out by Bergkvist [124], uncertainties due to the final state problem had to be taken into account as well. In order to further reduce the remaining uncertainties a novel type of experiment was proposed, in which solid state detectors were employed. In this way, no corrections for final-state effects were needed but, in principle, the lower resolution of solid-state detectors could be a disadvantage. In the experiment by J. J. Simpson [126], a measurement of the β-energy spectrum of tritium implanted at high energy into a Si(Li) X-ray detector was carried out. An extrapolated endpointenergy of (18,567 $\pm$ 5) eV was obtained, while the upper limit for the electron antineutrino rest mass was 65 eV (with 95% confidence). His concluding remarks were very interesting, giving some hints to further improve the limit on neutrino rest mass:

> Can the present limit on $m_{\overline{\nu}}$, from β-decay be improved? It has been argued in this paper that an inherent limitation on the accuracy imposed by atomic effects is at a much lower level than in the magnetic-spectrometer measurements, and that the main uncertainty therefore is statistical. The statistical accuracy is strongly influenced by the resolution, the radiation dose that the detector can tolerate, and the length of time which is used for recording the spectrum. In fact, if the present experiment were carried out for one tritium half-life, all other things remaining the same, the limit on $m_{\overline{\nu}}$, could be reduced to about 20 eV (90% confidence). (One might implant a dozen detectors and count for about a year, achieving again about 20 eV as a limit.) The resolution can be improved only marginally, so that at the moment work is in progress toward an experiment with higher count rate ([126], p. 639).

The experimental improvements devised since the 1980s and the upper limits values obtained for antineutrino (neutrino) rest mass will be the subject of a forthcoming subsection.

2.3. Orbital Electron Capture Experiments

The orbital electron capture process implies the capture of an electron from the K shell (or from the L shell) by the nucleus within an allowed transition, according to the reaction:

$$^{A}(Z+1) + e^{-}_{K,L} \rightarrow \, ^{A}Z + \nu, \tag{10}$$

where ${}^{A}Z$ is a nucleus with atomic number Z and mass number A. The process satisfies the conservation of energy principle:

$$W_\nu = M(Z+1) - M(Z) - E_r - B_{K,L}, \tag{11}$$

where W_ν is the neutrino energy (which includes the rest mass), $M(Z+1)$ and $M(Z)$ are the masses of the initial and final atoms, E_r is the recoil energy of the recoiling atom and $B_{K,L}$ is the binding energy of the K (or L) shell. In most neutrino experiments, the condition $W_\nu \gg (E_r + B_{K,L})$ holds on, which leads to the simplified expression $W_\nu = M(Z+1) - M(Z)$ for the conservation of energy.

As already anticipated in Section 2.1, the capture of an orbital electron by a radioactive nucleus was predicted for the first time by Wick [78] in 1934, while the first experimental observation was carried out in 1938 by Alvarez [80]. In 1948, Crane [16] pointed out the role of K-capture experiments in discriminating between the emission of single and multiple neutrinos:

> The measurement of the recoil in a K-capture process is the one experiment which can distinguish sharply between the emission of single and multiple neutrinos. If the single neutrino picture is correct, the momentum spectrum of recoils will be a line spectrum since the energy of the transformation is not shared between an electron and a neutrino but is taken by the neutrino alone. If no gamma-rays are emitted, the recoil spectrum will consist of a single line. In contrast, the multiple neutrino picture would, clearly, give a continuous distribution of recoil momenta. Second, recoil experiments can tell something about the angular correlation between the directions of emission of the electron and the neutrino ([16], p. 281).

Interestingly, once established, the emission of single neutrinos the angular correlation would be eventually obtained by non K-capture recoil experiments.

For the emission of a single neutrino, the kinetic energy of the recoiling atom could be provided by:

$$E_r = 140.2\frac{(W_\nu^2 - m_\nu^2)}{M}\ \text{eV}, \tag{12}$$

where W_ν is expressed in units of $m_e c^2$, the neutrino mass m_ν is given in terms of m_e and M is the mass of the recoiling atom; in general, E_r was found to be less than 100 eV for electron capture decay. Equations (11) and (12) were crucial for the determination of the neutrino rest mass: the mass difference between primary and secondary nuclei could be extracted from the threshold of the p, n reaction while an accuracy of 10^{-3} percent or less on W_ν and E_r was required in order to obtain an upper limit of one percent of the electron mass for the neutrino rest mass. Let us point out that in orbital electron capture experiments, the challenge was to measure the energy spectrum of the recoiling nuclei in order to extract information on the neutrino.

The use of ^{7}Be for an electron capture recoil experiment was first suggested by K. C. Wang [127] in 1942 on the basis of an extensive work on the properties of ^{7}Be carried out by L. H. Rumbaugh, R. B. Roberts and L. R. Hafstad [128]. The reaction for the formation of the isotope ^{7}Be was found to be ^{6}Li + ^{2}D $\rightarrow$ ^{7}Be + n at 3.3 MeV, with two decay modes: 90% according to ^{7}Be + e_K $\rightarrow$ ^{7}Li + ν at 0.87 MeV, 10% according to ^{7}Be + e_K $\rightarrow$ ^{7}Li* + ν at 0.396 MeV and ^{7}Li* $\rightarrow$ ^{7}Li + γ at 0.474 MeV. The values of the energy available for neutrino and gamma-ray emission above shown were measured by Haxby, Shoupp, Stephens, Wells [91] and by D. J. Zaffarano, B. D. Kern, A. C. G. Mitchell [129]. The first experiment based on ^{7}Be was carried out by Allen [90,130]. In principle, according to Allen [90,130], in an ideal recoil experiment, a well-defined energy of 58 eV would have to be found for the 90% of the ^{7}Li recoils, while a continuous distribution of energies ranging from 58 eV to zero was expected for the remaining 10%. In his experiment, the radioactive ^{7}Be was deposited on a platinum strip by means of a selective evaporation process. Most of the recoils became ionized when leaving the surface because the work function of platinum was larger than the first ionization potential for lithium. Furthermore, an electron multiplier tube for counting the recoil ions and a Geiger counter for gamma-ray counting were employed as detectors, while a retarding potential method was effective in measuring the maximum energy of the recoils. The resulting upper limits of the recoil curves were found to be about 10 V to 15 V lower than the expected value for a zero neutrino rest mass, but the discrepancy could be ascribed mainly to the work needed to extract the recoil ions from the platinum strip. By means of a separate experiment, the number of gamma-ray counts in coincidence with recoils counts was measured, leading to the conclusion that only a few recoils were caused by gamma rays alone. Thus, the observed recoils could be related to the emission of a neutrino with a rest mass close to zero [90,130]. A second ^{7}Be experiment was performed in 1951 by P. B. Smith and Allen [131], by using improved source preparation techniques and a new retarding grid structure for a better determination of the maximum energy of the recoils. In this way, a high surface efficiency was guaranteed, such that all the recoils were able to leave the surface. But in spite of these improvements, there was no agreement between the observed ^{7}Be recoil spectrum and the spectrum expected for the emission of single neutrinos. Furthermore, an upper endpoint of (56.6 ± 1.0) eV was found, a value matching the expected results (57.3 ± 0.5) eV. Unfortunately, in neither of these experiments, a definite conclusion could be drawn with respect to the question of single or multiple neutrino emissions. The third experiment conducted with ^{7}Be, by R. Davis [132], at odds with the previous ones used an electrostatic analyzer (with a two percent resolution) to determine the energy of the recoils. The recoil sources were carefully prepared in order to obtain a monolayer distribution of ^{7}Be on a lithium fluoride surface, which could guarantee a recoil spectrum free from surface effects. The observed spectra exhibited a peak near the high energy end of the spectrum, which led to the conclusion that the emission of a single neutrino took place within ^{7}Be electron capture decays. Furthermore, the endpoint energy value of this spectrum was (55.9 ± 1.0) eV.

The experimentalists' interest soon focused on ^{37}A as an optimal substance for neutrino recoils from electronic capture thanks to its properties. In fact, the decay mode by electronic capture was dominant and, without gamma-ray emission, recoils were produced mainly by neutrino emission. As a further interesting feature, argon is a monoatomic gas, so critical experimental issues related to surface and molecular effects were strongly suppressed. The decay of ^{37}A via electronic capture is described by the following process:

$$^{37}A + e^{-}_{K,L} \rightarrow \, ^{37}Cl + \nu, \tag{13}$$

characterized by a half-life of 34 days. The emission of a single neutrino is here assumed. For a zero rest mass of neutrino, the disintegration energy Q could be given by the ^{37}A$-$^{37}Cl mass difference. An estimate of Q, (816 ± 4) keV, was obtained by means of a ^{37}Cl (p, n) ^{37}A threshold measurement [133] together with the $n - p$ mass difference value (816 ± 4) keV [134]. Under these conditions and neglecting the binding energy of the orbital electron, the conservation of linear momentum between the recoil nucleus and the neutrino led to an energy of the nuclear recoil of (9.67 ± 0.08) eV. Furthermore, the emission of Auger electrons with a maximum energy of about 2500 eV was observed after the decay, resulting in multiple ionized recoiling atoms. The first neutrino experiment via orbital electron capture involving the isotope ^{37}A was carried out by G. W. Rodeback and Allen in 1952 [135], who determined the energy spectrum of the recoil nuclei via a time-of-flight measurement of the recoil ions (see the experimental apparatus in Figure 3 ([135], p. 447)). The source volume was maintained at a total pressure of about 10^{-5} mmHg, corresponding to a mean free path of 500 cm for argon atoms. The time-of-flight distribution was measured by means of a multichannel delayed-coincidence technique, showing a definite maximum time limit. Electron multiplier tubes were used as detectors for electrons and recoil ions. The shape and the extent of the distribution, in particular the main peak at about 7 µs, were found to be compatible with the expected results for mono-energetic recoils originating in the source volume. In fact, the absence of recoils with velocities less than the expected value 0.711 cm/µs was also observed, signaling the unique energy of recoil atoms. Zero and short-time coincidences were observed in addition to the above distribution, as a result of electron scattering associated with ^{37}A decays not originating in the source volume. This interpretation was consistent with the emission of single, mono-energetic neutrinos in correspondence with the main peak at about 7 μs.

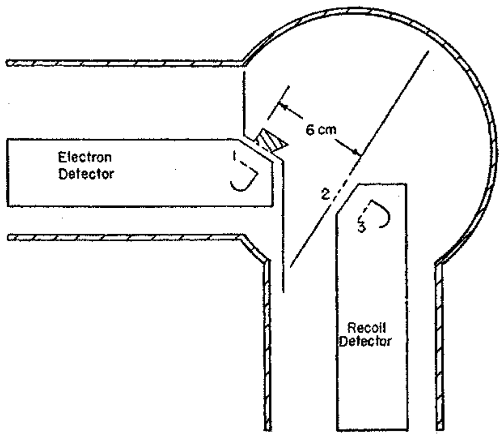

Figure 3. Schematic of the time-of-flight experimental apparatus. The shaded trapezoidal cross section in front of the grid 1 represents the effective source volume. The recoil ^{37}Cl ions arising from the source volume go to grid 2 through a field-free path, then accelerate by a potential difference of 4.5 kV and enter the ion counter (reprinted with permission from Ref. [135]. 2024, American Physical Society).

The charge distribution of the recoil ions originating from the ^{37}A decay was further investigated by Kofoed-Hansen [136] as well as by A. H. Snell and F. Pleasonton [137,138]. They both succeeded in performing very high-precision measurements. In particular, Kofoed-Hansen constructed a neutrino recoil spectrometer, which allowed him to study the motion of recoil ions in crossed electric and magnetic fields [136]. The spectrometer was built of a set of plane parallel condenser plates with a magnetic field parallel to the surface of the plates. The gas of decaying atoms filled the volume of the condenser. The recoil ions were detected by the current produced upon hitting the condenser plates. This current was measured in correspondence of a number of values of the ratio of the electric and magnetic fields. In turn the shape of the current plots allowed the extraction of the average kinetic energy of the recoil ions, whose measured value was (9.6 ± 0.2) eV in good agreement with the expected value for single neutrino emission, (9.67 ± 0.08) eV. The corresponding neutrino energy was (812 ± 8) keV, pointing to the presence of mono-energetic neutrinos [136]. On the other hand, Snell and Pleasonton followed a different experimental method, based on magnetic and electric deflection spectrometry [137,138]. Their apparatus consisted of a conical field-free source volume filled with argon at a total pressure of 2×10^{-5} mmHg or less. A small fraction of the recoil atoms within the source volume emerged from a hole with a diameter of 0.5 inch at the small end of the cone. The outgoing beam was analyzed by passing first through a magnetic field, and then through an electrostatic deflector. Finally, the ions were accelerated through 4600 V into a secondary electron multiplier for counting. The double, electric and magnetic deflection allowed the identification of the recoil ions both in terms of the charge-to-mass ratio and of energy. Furthermore, multiply charged recoils arose due to the Auger electron emission following the orbital electron capture. For the singly charged recoils, resulting from both *L*-capture and *K*-capture followed by *K* X-ray emission, the corresponding natural width at half-intensity amounted to 1.7 eV and could be fully ascribed to the thermal motion of the argon atoms. On the other hand, the natural width of the triply charged recoil line amounted to 2.5 eV and its origin had to be found partly in the thermal motion and partly in recoils from the emission of one 2300 eV *K* Auger electron. An estimate of the recoil energy using the peak corresponding to singly charged ions gave an average value of (9.63 ± 0.06) eV, in good agreement with the expected value (9.65 ± 0.05) eV, while the neutrino energy was (815 ± 2) keV (according to the threshold of the ^{37}Cl (p, n) ^{37}A reaction. Finally, from the momentum balance an upper limit of about 5 keV for the rest mass of the neutrino was extracted.

A further experiment on K-capture, based on 6.7-h ^{107}Cd, was initiated in 1941 by L. W. Alvarez, A. C. Helmholz and B. T. Wright [139] and then continued by Wright [140]. According to H. Bradt et al. [141], a K-electron capture to a metastable level in ^{107}Ag took place in 99.27% of the disintegrations so that a silver recoil ion of 7.9 eV was expected and the total energy available for the neutrino amounted to 1.25 MeV. In Wright's experiment, a ^{107}Cd active surface was prepared by a double vacuum distillation and exposed to a collector for a short time. In this way, the ^{107}Ag recoil atoms were collected and detected by counting the conversion electrons from the metastable ^{107}Ag* with an estimated efficiency of 8 percent. Furthermore, the collection efficiency did not depend on the sign of the electric field between the source and the collector, leading to electrically neutral recoils. As a consequence, the ^{107}Ag recoils were really the result of the K-capture process in the 6.7 h ^{107}Cd recoil rather than of the gamma rays and positrons produced in a small fraction of the transitions. In this respect, it is very interesting Crane's comment [16]:

> The energy which a neutral silver recoil must have to escape from the metal surface can be estimated reliably from the heats of vaporization of the metals involved, and is several electron volts. The maximum recoil energies obtainable from the x-rays and Auger electrons which follow the K-capture are only 0.003 eV and 0.22 eV, respectively. Therefore the fact that the recoils do escape from the surface, and that quantitatively the number collected is of the right order of magnitude, is strong evidence that momentum is acquired by the atom in accord with the neutrino hypothesis ([16], p. 283).

However, the possible presence of secondary processes as well as the lack of measurements of the energy distribution of the recoil atoms made Wright's results quite inconclusive.

In summary, orbital electron capture experiments based on ^{7}Be and ^{107}Cd did not provide a definite answer to the single neutrino hypothesis. Conversely, ^{37}A experiments confirmed the emission of single mono-energetic neutrinos, leading to an upper limit of 5 keV for the neutrino rest mass.

2.4. Pushing Limits below 50 eV: Recent Experiments on Tritium, Rhenium and Holmium

In this subsection, a brief account of recent experiments and methods aimed at a direct determination of the electron neutrino (antineutrino) rest mass is given, mainly focusing on the historical development of such methods rather than on the detailed technical issues, which can be found elsewhere [50–53,55].

By the end of the 1970s, the majority of direct neutrino mass measurements was carried out with tritium. Very soon neutrino mass effects were recognized to be small enough that it became mandatory to take into account a handful of competing effects such as atomic and molecular ones. As such, in order to push upper limits for the neutrino rest mass below the 50 eV limit the final-state problem had to be circumvented [122,123]. As further sources of systematic error, which needed careful control, there are the resolution function of the spectrometer, the energy loss of the electrons in the source and the experimental background.

The first experiment that obtained an upper limit below 50 eV was carried out between the late 1970s and the second half of the 1980s by a group from the Institute of Theoretical and Experimental Physics (ITEP) in Moscow [142–145]. As β-source a thin film of tritiated valine was employed, featuring a low tritium vapor pressure and a high specific activity. A novel high-luminosity spectrometer equipped with a toroidal magnet, the *Tretjakov spectrometer* , was introduced as well, allowing the ITEP group to find evidence for a nonzero neutrino mass between 14 eV and 46 eV at the 99% confidence level [142,143]. Assuming an atomic final-state spectrum (built of a ground state and a single excited state with an energy equal to 43 eV and a branching ratio equal to 0.3), a central value of 35 eV for the measurement of the neutrino mass was found, a result still dependent on the shape of the energy-loss spectrum from the source and on the resolution of the spectrometer. Further improvements[17] were obtained after 1981 by looking for possible sources of systematic errors and using a modified final-state spectrum, ranging from a central value of 33 eV together with the model-independent lower limit of 20 eV to a best-fit neutrino mass of 30^{+2}_{-8} eV and a new lower limit of 17 eV, and ending with a slightly decreased neutrino mass value of 26 eV [144,145].

The ITEP group results underwent close scrutiny by the scientific community. The first experiment aimed at exploring the same mass range as ITEP was carried out at the University of Zürich [146,147]. An upper limit of 18 eV on the neutrino mass was provided, but without confidence limits. A Tretjakov spectrometer was employed, but Zürich's apparatus was different from ITEP's one, allowing for a better resolution: the electrons were first decelerated and analyzed, then accelerated and detected. However, the whole procedure gave rise to a higher background level. Furthermore, a solid source of tritium implanted into the carbon was used [146], characterized by very low migration rates, which led to the presence of $C - T$ bonds. As such, the final state spectrum was approximated with that of tritiated methane, CH_3T, and modeled as a three-level spectrum, while the spectrometer resolution function was calculated by means of a Monte Carlo simulation. Zürich's results, which disproved ITEP's previous findings, were controversial, the critical issues being identified with the total resolution function used for data analysis and the model chosen for the energy-loss spectrum calculations [50]. A second experiment carried out in 1992 [147] succeeded in reducing systematic uncertainties. By using a thin source made of a self-assembling monolayer of tritiated hydrocarbon molecules and a modified Tretjakov spectrometer, an improved upper limit of 11 eV (with 95% confidence level) was derived for the electronic neutrino mass.

A further test of ITEP claims was performed by a group at Los Alamos National Laboratory (LANL) [148], who carried out an experiment based on the same magnetic spectrometer of the Tretjakov type. A novel gaseous molecular tritium (T_2) source was developed, which showed a number of interesting features: a well-understood final-state spectrum, a reduced energy loss and the absence of backscattering. Among the disadvantages, there were a low counting rate and a more complex experimental apparatus. The estimated upper limit on the electron antineutrino mass was 27 eV at the 95% confidence level. It would have been greatly improved later, in 1991, by the same group [149], thanks to the suppression of electron trapping in the source as well as to the replacement of the old detector module of the spectrometer with an octagonal array of Si microstrip detectors. The result was an upper limit of 9.3 eV (95% confidence level), which again did not support the ITEP claim [144,145]. Indeed, as pointed out later [150,151], the mass signal at ITEP was based on an overestimation of the energy loss correction and on a wrong measurement of the ^{3}He-T mass difference [152]. A similar windowless gaseous source of molecular tritium was employed also within the experiment carried out at Livermore National Laboratories (LNL), [153]. A negative value for the neutrino mass squared was obtained as a result of the best-fit procedure, probably due to the presence of an anomalous structure in the β-decay spectrum within a range of 55 eV near the endpoint.

More recent measurements were carried out at the Institute of Nuclear Studies (INS) in Tokyo with a magnetic spectrometer, reporting an upper limit of 32 eV (without mention of the confidence level) on the electron antineutrino mass [154]. A new source was employed, given by a Langmuir-Blodgett film of cadmium arachidate, which could be produced with a fixed thickness, equal to two molecules. Two different molecules were produced: the first one, partially tritiated, contained non-radioactive cadmium, while the second one, without tritium, was characterized by radioactive ^{37}Cd. These features allowed a very good quality determination of the energy-loss spectrum and a high-accuracy measurement of the total resolution function. Unfortunately, a significant uncertainty affected the final-state spectrum, putting a severe limit on the accuracy of the result. Further improvements were obtained in the subsequent years by addressing the following critical issues: the source alignment, the determination of the absolute energy scale and the total response function. The final result was an upper limit of 29 eV for the electron antineutrino mass [155]. Finally, the last run, performed after significantly enhancing the radioactivity of the source and the sensitive area of the β-detector, led to a new upper bound of 13 eV at 95% confidence level [156].

The above discussion clarifies the scenario of neutrino mass direct measurements since the first ITEP experiment and until the beginning of the 1990s. The measurements were carried out with Tretjakov-type magnetic spectrometers and were the subject of wide and controversial discussion. Without any doubt there was an impressive gain in sensitivity, but technical challenges and systematic errors were still a critical issue. The calculation of the final-state effects in complex molecules required a number of approximations, but a robust criterion for the assessment of the validity of these approximations was still lacking. Furthermore, there was no agreement on how to obtain the energy-loss contributions to the resolution function. Last but not least, LANL and LNL experiments produced large negative values of the neutrino mass squared $m^2_{\nu_e}$, demanding an explanation. These unphysical features were the result of an excess of events observed within the endpoint region and, later, would have been ascribed to problems in the calculation of the final-state distribution [157]. Indeed, a careful understanding of the role of molecular excitations in modifying the shape of the endpoint region of the β-decay spectrum is mandatory, because their distribution has been recognized as one of the possible sources of systematic error in experiments based on gaseous T_2 sources. In general, in a molecular β-decay a variety of final states are excited, namely translational, electronic, rotational and vibrational states, which make the calculation of the final state distribution very cumbersome. Some ab initio calculations of the molecular excitations were carried out for T_2 β-decay [158,159], while continuum states had been successfully taken into account by P. Froelich et al. in 1993 [160]. These findings allowed the elimination of the large negative value of $m^2_{\nu_e}$ in both LANL and LNL experimental results [158]. Negative neutrino mass squared values would have been reported later also by other experiments, such as those by Mainz [161,162] and Troitsk [163,164] groups, but their sources were identified in a number of different systematic errors. In particular, large negative values of $m^2_{\nu_e}$ were obtained when observing data within a range of 500 eV below the endpoint of the β-spectrum, while disappearing upon limiting the analysis to a very small range below the endpoint. The effect was recognized to be due to a missing energy loss process, whose origin was very different in either experiment [165,166].[18]

The beginnings of the 1990s marked a new era in experiments aimed at direct neutrino mass determination via β-decay spectrum: a novel electrostatic spectrometer entered the scene, the MAC-E Filter (Magnetic Adiabatic Collimation with an Electrostatic Filter), characterized by an enhanced energy resolution and a very high luminosity at a low background with respect to the previous Tretjakov-type magnetic spectrometers. These features made the MAC-E Filter appealing for the measurement of the neutrino mass via the investigation of the endpoint region of a β-decay spectrum. The device, introduced in 1976 by T. Hsu and J. L. Hirshfield [167] and further developed by G. Beamson et al. [168] and P. Kruit and F. H. Read [169], was finally tuned for a proper application to tritium experiments by Mainz and Troitsk groups independently [170,171]. It combined a retarding-field analyzer with a magnetic field for collimation. The basic working principle is shown in Figure 4 (see Ref. [74], p. 2).

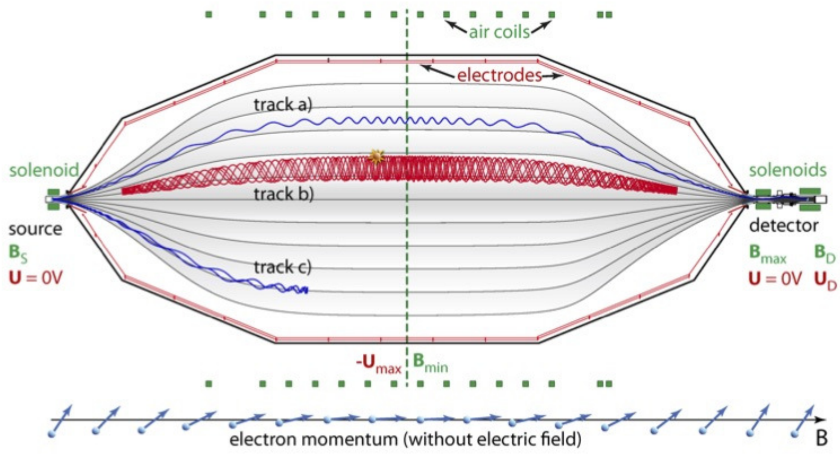

Figure 4. The basic working principle of the MAC-E Filter (reprinted with permission from Ref. [74]. 2024, IOP Publishing).

Interestingly the device was characterized by a 2π solid angle acceptance. A magnetic guiding field was produced by two superconducting solenoids, so the electrons emitted by the tritium source in the left solenoid were guided to perform a cyclotron motion along the magnetic field lines into the spectrometer. The gradual decrease in the magnetic field (by several orders of magnitude), while the electrons traveling towards the center of the spectrometer, changed most of the cyclotron energy into longitudinal motion. Furthermore, an electrostatic barrier placed in the center of the spectrometer analyzed the parallel beam of electrons, selecting only those with sufficient energy to pass. Finally, these electrons accelerated, entered a high magnetic field and were detected [74]. The energy resolution was given by the ratio of the magnetic fields within the source and the spectrometer, and ultimately by the choice of the accepted pitch-angle range [172].

MAC-E Filters were adopted by the two tritium β-decay experiments carried out at Mainz [161,162,165] and at Troitsk [163,164,166], featuring an energy resolution of 4.8 eV and 3.5 eV, respectively. The two experimental setups were different mainly in the tritium sources. Indeed at Mainz, a thin film of molecular tritium quench-condensed on a cold graphite substrate was used, while the Troitsk experiment chose a windowless gaseous molecular tritium source very similar to those employed at previous LANL and LNL experiments. Both experiments showed a limit at about 2 eV, which coincided with the sensitivity limit of the devices employed. Since the first run of the Mainz experiment in 1993, various upgrades of the apparatus allowed for a huge enhancement of the statistical quality of the data by long-term measurements, a lower and stabilized background and an improvement of the signal-to-background ratio by a factor of 10. Finally, a careful investigation led to a significant reduction in systematic uncertainties [165]. The data analysis of the small region (with a range of 70 eV) below the endpoint gave the result $m^2_{\nu_e} = (-0.6 \pm 2.2 \pm 2.1)$ eV^2, corresponding to an upper limit of $m_{\nu_e} < 2.3$ eV (at 95% confidence level) [165]. Concerning the Troitsk experiment, since 1994 the observation of a small anomaly in experimental spectra was reported, starting at about a few eV below the endpoint energy E_0 of the β-spectrum [163]. This anomaly showed as a narrow line in the primary spectrum with a relative intensity of about 10^{-10} of the total decay rate. It would have been corrected later, leading to the final result [166] $m^2_{\nu_e} = (-0.67 \pm 1.89 \pm 1.68)$ eV^2, which led to an upper limit of $m_{\nu_e} < 2.05$ eV (at 95% confidence level) [166].

Currently, the aim of the next generation direct neutrino mass experiments is to further improve the m_{ν_e} sensitivity by a factor of 10 the current upper limit of about 2 eV. Huge experimental efforts have been carried out towards this goal, culminating in the design of the Karlsruhe Tritium Neutrino (KATRIN) experiment [173]. Both MAC-E Filter and tritium process technology have been further developed until reaching their limits within KATRIN.[19] The general criteria which have to be satisfied include major improvements in energy resolution ΔE (up to a value of 0.93 eV) and background rate close to the endpoint (up to $< 10^{-2}$ count per second), careful control of systematic uncertainties (a reduction of one order of magnitude is mandatory), an increased source strength by a factor of 100 and of the measurement time by a factor of 10. Hence, the main components of the 70 m long KATRIN apparatus [74,172–174] are a high luminosity gaseous tritium source, which delivers 10^{11} decay electrons per second; an electron transport and tritium eliminating section; an electrostatic MAC-E Filter pre-spectrometer; a large electrostatic main spectrometer, also of MAC-E Filter type; a segmented Si-PIN diode array devoted to the counting of transmitted electrons. A schematic overview is shown in Figure 5 (see Ref. [74], p. 5).

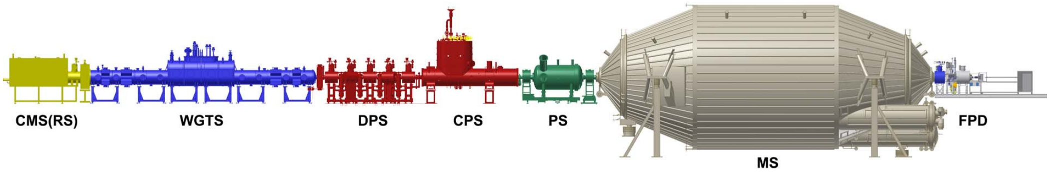

Figure 5. Schematic overview of KATRIN experimental apparatus: calibration and monitoring system (CMS), windowless gaseous tritium source (WGTS), differential pumping section (DPS), cryogenic pumping section (CPS), pre-spectrometer (PS), main spectrometer (MS), focal plane detector (FPD) (reprinted with permission from Ref. [74]. 2024, IOP Publishing).

The experiment started in 2018, while the first results were delivered in 2019; in particular, an upper limit of 1.1 eV (at 90% confidence level) on the absolute neutrino mass scale was obtained [174]. The experimental progress achieved over the years in measuring neutrino mass with β-decay can be visualized in Table 1, where the results of the main experiments involving tritium are collected.

Table 1. Results of the main neutrino mass experiments with tritium.

Group and Date	Spectrometer	Mass (eV)
Curran et al., 1949 [111]	Proportional Counter	<1000
Hanna, Pontecorvo 1949 [112]	Proportional Counter	<500
Langer, Moffat 1952 [114]	Magnetic	<250
Hamilton et al., 1953 [117]	Electrostatic	<200
Daris, St. Pierre 1969 [121]	Magnetic	<75
Bergkvist 1972 [122,123]	Magnetic	<55
ITEP 1980 [142,143]	Magnetic	$=30 \pm 16$
Simpson 1981 [126]	Si(Li)	<65
Zurich 1986 [146]	Magnetic	<18
ITEP 1987 [145]	Magnetic	$=30^{+2}_{-13}$
LANL 1987 [148]	Magnetic	<27
INS 1991 [156]	Magnetic	<13
LANL 1991 [149]	Magnetic	<9.3
Mainz 1993 [161]	MAC-E	<7.2
Troitsk 1994 [163]	MAC-E	<4.35
Mainz 2005 [165]	MAC-E	<2.3
Troitsk 2011 [166]	MAC-E	<2.05
KATRIN 2020 [174]	MAC-E	<1.1

The KATRIN experiment is currently running towards its ultimate goal (an upper limit on the electron neutrino mass close to 0.2 eV), while novel technologies such as the Cyclotron Radiation Emission Spectroscopy (CRES) [175] began to be applied to the neutrino mass problem, as in the Project 8 experiment, aiming to a sensitivity level of $m_{\nu_e} < 40$ meV at 90% confidence level [176,177]. In principle, in order to obtain sub-eV sensitivity, a high-precision spectroscopy of low-energy electrons is mandatory. This task can be accomplished only by pursuing new experimental strategies since the existing electromagnetic techniques are already at the limit of their sensitivity. In this respect, CRES technology [175,178,179] is very promising; it is based on the coherent radiation released during cyclotron motion as a tool to extract energy from electrons emitted within tritium β-decay. As such, its key features are the non-destructive measurement of a frequency and an extremely low background level, which are expected to guarantee a very high resolution and accuracy. As a further bonus, the extraction of electrons from the source and the source–detector separation is no longer needed, which is at odds with usual spectrometer techniques (as employed in KATRIN [74]).

Among the viable isotopes to address direct neutrino mass determination, there are Rhenium, ^{187}Re, and Holmium, ^{163}Ho, which feature a Q-value lower than that of tritium. While for Rhenium the low Q-value (2.5 keV) is outweighed by the forbidden nature of the β-decay, requiring calorimetric measurements [180], Holmium decays via electron capture by emitting neutrinos [181].

The first-order forbidden nature of the transition characterizing the β-decay process for ^{187}Re strongly modifies the phase space of the β-electrons near the endpoint. As a consequence, the lifetime becomes very long (i.e., 4.12×10^{10} yr) requiring a huge amount of target material to observe enough decay events with energies close to the endpoint. The first ^{187}Re β-decay experiments were carried out in the 1960s by R. L. Brodzinski and D. C. Conway [182] and by E. Huster and H. Verbeek [183] using proportional counters. From both measurements, a Q-value of 2.6 keV was extracted but no neutrino mass measurements were reported. The idea of using microcalorimeters to improve sensitivity and to be able to detect the neutrino mass signal was pioneered by two experimental groups at Genoa (MANU) [184,185] and Milan (MiBETA) [186,187]. MANU experiment [184,185] employed a single metallic rhenium crystal as a self-contained absorber, taking into account the superconducting nature of rhenium below 1.7 K. These conditions led to the exponential suppression of the electronic contributions to the heat capacity, leaving out only lattice contributions. Upon cooling down the system at very low temperatures (usually below 100 mK), the heat capacity was strongly reduced leading to a high energy resolution and hence to a high accuracy endpoint measurement. The drawbacks of this approach could be traced back to quasi-particle trapping phenomena at low temperatures, whose effect was a reduction in the event rate with consequent rise and decay times of the order of 1 ms and several tens of ms, respectively. The net result was a limit on the amount of activity allowed per absorber crystal. On the other hand, the MiBETA experiment [186,187] worked with an array of $AgReO_4$ absorbers to circumvent issues related to quasi-particle trapping in superconductors, while obtaining the same suppression of electron-based noise as MANU experiment. Starting from the analysis of the spectrum near the endpoint, both experiments were able to extract an upper limit on the electron neutrino mass lower than 20 eV at 90% confidence level (i.e., $m_{\nu_e} \leq 19$ eV (MANU) and $m_{\nu_e} \leq 15$ eV (MiBETA)). A novel calorimetric experiment using rhenium is currently under study, the Microcalorimeter Arrays for a Rhenium Experiment (MARE), aimed to push the sensitivity to neutrino mass to the sub-eV limit [180,188].

The low Q-value (about 3 keV) characterizing the decay via electron capture of ^{163}Ho to ^{163}Dy made holmium very attractive as well for a neutrino mass measurement [189]. After the failure of a proposal based on the theory of subshell ratios in heavy nuclei [190], a different approach was put forward by A. De Rujula [191], relying on the phenomenon of internal bremsstrahlung in electron capture (IBEC). Here, the endpoint shape of the corresponding continuous spectrum of photons would be modified by the neutrino mass, in analogy with β-decay spectrum. Another key point of De Rujula's approach was his suggestion of a calorimetric detection technique, which is currently used today in ^{163}Ho experiments. The first ^{163}Ho neutrino mass experiment based on the IBEC phenomenon was carried out in 1987 [192], obtaining an upper limit of 225 eV on the neutrino mass. An upper limit of 460 eV was established in 1994 [193] by means of a measurement of subshell ratios, which circumvented previous drawbacks [190]. After these initial attempts, the experimental work focused on microcalorimetric techniques, based on the whole capture and heat conversion of photon and electron produced via de-excitation of the ^{163}Dy. Here, the endpoint of the energy spectrum coincides with the Q-value, except for small lattice corrections. As a result of a long-lasting experimental effort, the upper limit on the neutrino mass has been gradually lowered from the initial 225 eV to a current value of 150 eV [194]. Three ^{163}Ho experiments, based on the microcalorimeter technique, are currently ongoing, ECHo [194], HOLMES [195] and NuMECS [196], aiming to reach a sub-eV sensitivity.

3. Neutrinoless Double β-Decay

As outlined in the introduction, probing the lepton charge conservation and the Dirac or Majorana nature of massive neutrinos are a challenge in the actual landscape of particle physics. The huge efforts carried out in an attempt to measure the neutrino mass, or to set an upper limit to its value, could not be able to say anything about the very nature of neutrinos. Also, the shape of the β-decay spectrum in the vicinity of the endpoint, which depends on the neutrino mass, could not provide information in this respect. Over the years, the phenomenon of double β-decay gained a wide consensus as a viable strategy to probe the nature of neutrinos. If the neutrino is a Dirac particle, then it is different from the antineutrino. Thus, the double β-decay can be viewed as a two-step process:

$$(A,Z) \rightarrow (A,Z+2) + e^- + e^- + \overline{\nu}_e + \overline{\nu}_e, \tag{14}$$

whose net result is the change of two neutrons into two protons accompanied by the emission of two electrons and two antineutrinos. The electrons give rise to a continuous energy spectrum but the process has an extremely long half-life (about $10^{18} \div 10^{19}$ yr for a kinetic energy release of 4 MeV), which makes its detection very challenging. However, its detection could be feasible in nuclei characterized by a forbidden β-decay while allowing a double β-decay process.

On the other hand, if Majorana's hypothesis [12] is fulfilled, only one type of neutrino exists (i.e., the neutrino coincides with its antiparticle) and the double β-decay process occurs according to a different two-step scheme:

$$(A,Z) \rightarrow (A,Z+2) + e^- + e^-. \tag{15}$$

Here, a virtual neutrino is released in the first step and absorbed in the second step, resulting in the emission of two electrons only, while two neutrons change into two protons. Upon neglecting the energy of the recoiling nucleus, the whole energy available for the transition is carried by electrons, showing up in a sharp line spectrum at odds with the continuous shape of the previous case. The estimated half-life for such a process is very long as well, currently higher than 10^{26} y in all practical isotopes.

Majorana's neutrino hypothesis allows also for the occurrence of the related phenomenon of resonant neutrinoless two-electron capture, according to the following scheme:

$$e^- + e^- + (A,Z) \rightarrow (A,Z-2)^{**}. \tag{16}$$

Here, e^- are bound electrons while the nucleus and the electron shell of the neutral atom $(A,Z-2)^{**}$ are in excited states. Two protons within a nucleus capture a bound electron from the electron shell, turning into two neutrons via the exchange of a Majorana neutrino. The sensitivity of this process to Majorana neutrino masses is significantly lower than that of neutrinoless double β-decay but could be improved by a resonance enhancement effect, while the corresponding estimated half-life is approximately equal to 10^{19}–10^{22} yr.

While two-neutrino double β-decay ($2\nu\beta\beta$) has been observed in several isotopes, the neutrinoless double β-decay ($0\nu\beta\beta$) and two-electron capture ($0\nu 2EC$) processes are still waiting for an experimental confirmation. In the case of $0\nu\beta\beta$-process, current efforts are devoted to careful control of the experimental background to match the extremely low levels required for sensitivity. As such, increasingly advanced experimental technologies and data analysis methodology are requested, leading eventually to ton-scale detectors.

Concerning the $0\nu 2EC$, the challenging points are a lower relative abundance of the isotopes of interest (usually lower than 1%) and a lower detection efficiency for the most energetic peak of the $0\nu 2EC$-spectrum due to the emission of a γ-cascade. However, the resonance enhancement effect might improve the situation and pave the way towards the realization of large-scale experiments.

A successful $0\nu\beta\beta$- (as well as $0\nu 2EC$-) experiment would be of seminal importance: indeed establishing the Majorana nature of massive neutrinos would have far-reaching implications for the neutrino mixing theory; in particular, a better understanding of the mechanism of generation of the baryon asymmetry of the Universe is expected.

The aim of this section is to retrace the history of this huge experimental endeavor starting from the first theoretical predictions of the double β-decay process.[20]

3.1. Early Theoretical Issues

The possibility of a two neutrino double β-decay (14) was put forward for the first time in 1935 by M. Goeppert-Mayer [204], who found that some even–even nuclei could undergo decay into a lighter nucleus with the release of two electrons and two neutrinos. This happened while the normal β decay was forbidden. In this respect, she observed the following:

> A disintegration with the simultaneous emission of two electrons and two neutrinos will then be in strong analogy to the Raman effect, or, even more closely, to the simultaneous emission of two light quanta, and can be calculated in essentially the same manner, namely, from the second-order terms in the perturbation theory. The process will appear as the simultaneous occurrence of two transitions, each of which does not fulfill the law of conservation of energy separately ([204], p. 512).

Thus, she carried out a second-order perturbative calculation according to Fermi theory [7–10] to find the probability of simultaneous emission of two electrons and two neutrinos, providing also a numerical evaluation for the $Z = 31$ case ($P \sim 10^{-20}$ yr^{-1}). This value was indeed very small, as later pointed out by W. H. Furry: "The probability of double β-disintegration was calculated some years ago by Goeppert-Mayer on the basis of the Fermi theory. The result obtained was extremely small, corresponding to a lifetime of the order of 10^{25} years in the case of two isobars whose masses differ by 0.002 mass unit and whose atomic numbers differ by two units" ([57], p. 1184). Interestingly, at the end of the article, she acknowledged E. Wigner for suggesting the problem ([204], p. 516).

In 1937, E. Majorana published his celebrated paper *Teoria Simmetrica dell'Elettrone e del Positrone* [12], where he suggested the possibility of a particle-antiparticle symmetry, which allowed him to completely reformulate Dirac's electron–positron theory and to build up a new theory for particles without electric charge. The proposal of an identity between a matter particle and its antiparticle immediately asked for a physical realization of this attractive possibility. According to Majorana, a successful candidate could be the elusive particle postulated by Pauli [1,2] and then employed by Fermi to explain the puzzling features of β-decay and to construct his successful theory [7–10]. Thus, the concept of Majorana neutrino entered the scene and very soon would have been recognized as a viable alternative to Dirac neutrino. In this respect, a passage of Furry's 1938 paper [205] is very enlightening:

> Majorana has recently shown by using a special set of Dirac matrices that the symmetry properties of the Dirac equations make possible the elimination of the negative energy states in the case of a free particle. [...] Majorana also showed how his ideas can be applied in the theory of the neutral particle to obtain a formalism essentially different from that of the ordinary Dirac theory. Qualitatively the difference appears in the number of states having the same momentum. In the Dirac theory as used at present there are four such states, corresponding to two alternatives for the spin orientation and to the possible existence of both the particles in question and their "antiparticles"? e.g., neutrinos and antineutrinos. In the Majorana theory there are just two states for a given momentum, corre-

sponding to the two possibilities for the spin: there are no "antiparticles" and, in the final formulation, no mention of negative energy states. [...] For the neutrino, however, the Majorana theory is *a priori* just as acceptable as the ordinary Dirac theory. It is interesting to find that it is possible to accomplish all the purposes for which the neutrino theory was devised, including the discussion of both electron emission and positron emission, without the introduction of antineutrinos ([205], p. 56).

A few months Later, the deep consequences of Majorana's neutrino hypothesis were investigated by G. Racah [206], who showed that Majorana's theory could not hold for neutrons, due to their magnetic moment. In particular, he showed that a Majorana neutrino (such that $\overline{\nu} = \nu$) emitted in a β-decay can give rise to an electron via the inverse β-decay reaction:

$$\nu + (A, Z+1) \rightarrow (A, Z+2) + e^{-}. \tag{17}$$

This was impossible for a Dirac neutrino! In fact, in an inverse β-decay a Dirac antineutrino produced via β-decay would give rise to a positron in the final state. Hence, according to Racah the study of inverse β-decay induced by neutrinos could be a viable strategy to discriminate between a Dirac and a Majorana particle.[21] Racah and Majorana's ideas were closely analyzed by Furry [205], but his conclusions on the real possibility to experimentally distinguish between Dirac and Majorana neutrinos were pessimistic:

In the ordinary theory one type of β-decay involves the emission of neutrinos and the other the emission of antineutrinos, but in the Majorana theory use is made of neutrinos only. It should be possible to settle which theory is preferable by considering processes in which neutrinos are absorbed as well as emitted, but actually this does not seem feasible at present. Differences would presumably appear in the results of using the light particle fields to account for the forces between heavy particles, but this part of the subject is in such an unsatisfactory state owing to divergence difficulties that it seems to offer no hope of a decision, and indeed it seems quite doubtful that nuclear forces are to be explained in this way. Another possibility of deciding between the two theories is offered in principle by the phenomenon of β-decay with *absorption of* a light neutral particle instead of its *emission*, the β-ray accordingly having *more* energy than the limit of the spectrum instead of less. Here, as Racah has remarked, there is an obvious qualitative difference between the two theories. On the ordinary Dirac theory, a positron emitter can be "stimulated" only by an electron emitter, and vice versa, but on the Majorana theory any emission may "stimulate" any other emission, whether of the same or of opposite type. But since the cross section of a radioactive nucleus for capture of a neutrino is of order of magnitude between 10^{-40} and 10^{-50} cm^2, it seems unlikely that this effect, which would not only serve to decide the question of the existence of antineutrinos but would provide experimental evidence of the best sort for the neutrino hypothesis itself, can ever be observed ([205], p. 67).

Indeed, in 1938, there were no intense sources of neutrinos available. One year later, in a subsequent article [57], Furry themself put forward a decisive argument that opened new experimental perspectives: the neutrinoless double β-decay process (Equation (15)) could only take place when neutrinos are Majorana particles, while the same process would be impossible for Dirac neutrinos. He calculated the transition probability for such a process under the Majorana hypothesis by taking a zero neutrino mass and using various Fermi and Konopinski–Uhlenbeck [82] interactions. The corresponding order of magnitude was greater than what was expected for a two-neutrino process by a factor of about 10^5 to 10^{15}. A direct comparison with Goeppert-Mayer results for the transition probability of the two-neutrino process [204] was performed in the case $Z = 31$, finding a probability value about 10^6 times that obtained by Goeppert-Mayer and, thus, a shorter half-life.

Later, in 1952, in a work by E. Caianiello [208] the issue of the nature of neutrino was addressed again, pointing out its possible role for an explanation of double β-decay phenomena, but the author's findings contradicted Majorana hypothesis:

> We prove here that the condition of self charge-conjugation is incompatible with the usual invariance requirements; identity of a field with its charge-conjugate is impossible, because they transform differently under space reversal. Clearly, this suffices to rule out the Majorana theory ([208], p. 564).

Interestingly, the conclusions hinted at the possibility of an interpretation of double β-decay phenomena also without Majorana neutrinos.

> Coming back to physics, we wish to point out, finally, that the rejection of the Majorana theory for the neutrino would not forbid the interpretation of double beta-decay phenomena, should they be definitely proved to occur ([208], p. 565).

The experimental efforts carried out since 1948 to look for double β-decay and related processes will be the subject of the following subsection.

3.2. Experiments

The early experiments devoted to looking for double β-decay processes aimed at providing an answer to the question of the Dirac or Majorana nature of the neutrino. Indeed, the existing theoretical estimates gave a half-life of 10^{15} yr for the $0\nu\beta\beta$-decay and a Majorana neutrino, while a half-life of 10^{20} yr was obtained for a $2\nu\beta\beta$-decay process involving Dirac neutrinos [57,204].

The first experiment on double β-decay was carried out in 1948 by E. L. Fireman [209], who used two counter units, each built of two end-window Geiger counters connected to a coincidence circuit, and obtained a half-life higher than 3×10^{15} yr for $^{124}_{50}$Sn. In a second instance of the same experiment, conducted one year later on the same isotope, he found results compatible (in his opinion!) with a double β-decay without neutrinos and estimated a half-life between 4×10^{15} yr and 9×10^{15} yr [210]. But his conclusion was soon disproved by more sensitive experiments on various isotopes carried out within a couple of years, between 1951 and 1953, and claiming positive results [211–214], which in turn would have been disproved by subsequent experiments.[22] For instance, the experiment by M. I. Kalkstein and W. F. S. Libby [211] gave a half-life for double β-decay in ^{124}Sn longer than 10^{17} yr, a result confirmed also by Fireman and Schwarzer [213], who made a comparison with the results reported in 1948 [209] and commented "The previous result may have been caused by a small trace of an impurity having a coincidence activity in the enriched sample" ([213], p. 453). Indeed, significant events from double β-decay sources had a very high probability of being masked by ordinary decays from small traces of radioactive elements, because of their significantly longer half-life. The same period was marked by the beginning of the investigation of the following processes, $((A, Z) \to (A, Z-2) + e^+ + e^+$ as well as $e^- + (A, Z) \to (A, Z-2) + e^+$, both related to the double β-decay phenomenon, albeit with negative results [216,217]. In general, these early experiments were conducted by using sophisticated techniques and a variety of detectors, ranging from Geiger and proportional to scintillation counters, to Wilson chambers and nuclear emulsions, while the sources were mainly enriched isotopes such as ^{48}Ca, ^{94}Zr, ^{96}Zr and ^{124}Sn. The experimental set up was equipped with passive and active shielding and placed underground in order to suppress cosmic ray background. But, despite these huge efforts, the sensitivity was still about $10^{17} \div 10^{18}$ yr.

In 1955, R. G. Winter [218] theoretically investigated the possibility of a neutrinoless two-electron capture to an excited level of the daughter nucleus to occur with increasing probability under the resonance conditions. The possible resonant enhancement of the $0\nu 2EC$-process would have been pointed out again in the early 1980s [219,220], soon followed by the analysis of near-resonant $0\nu 2EC$-processes by J. Bernabeu et al., who also provided a list of nuclide pairs as possible candidates for degeneracy [221].

The first geochemical experiment dates back to 1949 and was carried out by M. G. Inghram and J. H. Reynolds [222]. They looked for the process ^{130}Te $\rightarrow$ ^{130}Xe + e^- + $e^-(+\overline{\nu}+\overline{\nu})$, which required the separation of xenon from ancient minerals (up to several billion years) followed by its isotope analysis. The occurrence of double β-decay would be signaled by an excess of ^{130}Xe, whose detection made it possible to measure its half-life. A lower bound of 8×10^{19} years was obtained, a clear indication of a higher sensitivity with respect to that of experiments made with counters. In 1950, Inghram and Reynolds [223], by the same experimental technique, detected the double β-decay of ^{130}Te finding a half-life of 1.4×10^{21} years. Their result was met with skepticism from the scientific community, but it would have been fully acknowledged about two decades later as a true detection of the $2\nu\beta\beta$-process. But in 1950 also, the first radiochemical experiment took place, based on the isotope ^{238}U [224]. The idea was to look for ^{238}Pu as a double β-decay product of ^{238}U. The experimental procedure required taking 14 kg of very pure uranium oxide and then extracting and separating the plutonium fraction by chemical methods. The final sample was introduced into an alpha pulse analyzer apparatus in order to detect the presence of 5.51 MeV α-particles of ^{238}Pu. The resulting ^{238}Pu α-particles counting rate gave a half-life of ^{238}U for simultaneous emission of two β-particles greater than 6×10^{18} years.

In 1957–1958, the discovery of parity violation in the β-decay [22] as well as the two-component neutrino theory by Lee and Yang [23], Landau [24] and Salam [25] supported the assumption of massless nature of the neutrino and contributed to cast a shadow on Majorana theory. This attitude is vividly expressed in Lee and Yang's seminal work:

> We shall now discuss some general properties of this neutrino field:
>
> (A) In this theory it is clear that the neutrino state and the antineutrino state cannot be the same. A Majorana theory for such a neutrino is therefore impossible.
>
> (B) The mass of the neutrino and the antineutrino in this theory is necessarily zero. This is true for the physical mass even with the inclusion of all interactions. To see this, one need only observe that all the one-particle *physical* states consisting of one neutrino (or one antineutrino) must belong to a representation of the inhomogeneous proper Lorentz group identical with the representation to which the free neutrino states discussed above belong. For such a representation to exist at all, the mass must be zero ([23], p. 1672).

Then, the universal $V - A$ theory of weak interactions [27,28] led to a key consequence: the probability of occurrence of $0\nu\beta\beta$-decay could be much smaller than that related to the $2\nu\beta\beta$-process. Finally, the possibility of neutrino oscillations and mixing advocated by Pontecorvo [30–32] and further developed by Maki, Nakagawa and Sakata [36] strongly supported the picture of massive neutrinos but could not provide an answer to the issue of the very nature of neutrinos.

This was the research landscape on neutrino physics at the beginning of the 1960s, when E. Greuling and R. C. Whitten performed the first calculation of the probability of $0\nu\beta\beta$-decay within the Majorana neutrino theory, without assuming lepton number conservation [225]. Their work suggested the experimental search for $0\nu\beta\beta$-decay as a means to check the validity of the lepton number conservation law, as clearly stated in the conclusions:

> We would like to suggest that further attempts to measure the double beta-decay process may be "indeed ... worth-while." The discovery that the law of conservation of parity is violated in the weak interactions has led us to believe in the completely longitudinally-polarized "two-component" neutrino and the consequent law of lepton conservation in the weak interactions. It is certainly worth-while to measure the double beta-decay process for in doing so it is possible that someone will find the answer to the question we raise, "Are leptons conserved?" If only the two-neutrino mode of decay is found to occur in nature, then lepton conservation becomes much more firmly established than is now evident. If the neutrino less mode of decay is found to occur in nature, the principle

> of lepton conservation is not valid, more will be learned about the interaction [...], and possibly a lower limit on the neutrino's mass could be established ([225], p. 530).

Due to the latent skepticism towards Majorana's hypothesis and the pessimistic predictions of the probability of occurrence of $0\nu\beta\beta$-decay, only a few experiments were carried out in the 1960–1980 period, among which those by E. der Mateosian and M. Goldhaber [226] and E. Fiorini et al. [227,228]. Mateosian and Goldhaber for the first time obtained a sensitivity of 2×10^{20} yr in novel counter experiments based on ^{48}Ca. As a key innovative technique, the enriched source under study was exactly the working substance of the detector [226]. On the other hand, the experiment by Fiorini and collaborators obtained a lower bound of 3×10^{20} yr on the $0\nu\beta\beta$-decay of ^{76}Ge by using Ge(Li) detectors [227]. The result was significantly improved by the same group in 1973, finding the new lower bound 5×10^{21} yr [228]. Remarkable experiments were also conducted by C. S. Wu and his group by using an apparatus built of a streamer chamber in a magnetic field followed by plastic scintillators. Remarkable lower bounds were obtained on $0\nu\beta\beta$-decay for isotopes characterized by high energy 2β-transitions, i.e., 2×10^{21} yr for ^{48}Ca (4.272 MeV) [229] and 3.1×10^{21} yr for ^{82}Se (2.9952 MeV) [230]. Finally, since the second half of the 1960s, geochemical experiments with ^{130}Te, ^{82}Se and ^{128}Te were carried out as well, confirming previous results on ^{130}Te obtained in 1950 [231,232] and detecting for the first time the $2\nu\beta\beta$-decay with ^{82}Se [233] and ^{128}Te [234].

The huge theoretical developments starting at the end of the 1970s contributed to a revival of the interest in Majorana's hypothesis, and hence towards the experimental detection of its expected fingerprint, the $0\nu\beta\beta$-decay. In particular, the phenomenological neutrino mixing theory set up by Bilenky and Pontecorvo led to the introduction of the so-called Dirac and Majorana mass term [235], which is at the basis of both the seesaw mechanism of neutrino mass generation and the formulation of grand unified theories (GUTs) [236]. Within the GUTs scenario, massive Majorana neutrinos appeared naturally as a consequence of the breakdown of the symmetry associated with lepton charge conservation. These developments marked the beginning of a new era in which the neutrino mass would have been considered as a signature of a new physics beyond the Standard Model. Furthermore, the ITEP group [142–145] claimed the detection of a neutrino mass of about 30 eV within a β-decay experiment based on tritium, while a neutrino with a mass of tens of eV was considered as a viable dark matter candidate in a period in which the first theories on the origin of the baryon asymmetry of the Universe based on leptogenesis were put forward [237].

Meanwhile, the experimental efforts towards the detection of $0\nu\beta\beta$-decay started to increase at a rapid pace, boosted also by the use of deep underground detectors built of low background materials and equipped with passive and active shielding. A significant reduction in background was obtained, leading to a further increase in sensitivity, and then to half-life limits of about $10^{23} \div 10^{25}$ years. Since 1998, the successful observation of neutrino oscillations in experiments involving neutrinos from various sources, ranging from atmospheric [38–40] and solar ones [41–47] to reactors [48], took place, clearly pointing to a massive neutrino, with far-reaching implications in particle physics. As a consequence, the interest in the $0\nu\beta\beta$-decay phenomenon grew up more an more because the perspectives were amazing. If the neutrinos will be shown to be Majorana particles, then an answer to a number of fundamental questions is expected: the neutrino mass spectrum and hierarchy type (normal, inverse, quasi degenerate); the absolute scale of the neutrino mass; the Majorana phases within the PMNS matrix; the existence of sterile neutrinos.

Without any doubt, decades of experimental attempts as well as theoretical investigations testify that the detection of $0\nu\beta\beta$-decay is an extremely challenging endeavor. Indeed no one has ever been able to observe it! The process is very slow, so current experimental efforts are mainly devoted to improving sensitivities more and more. While a variety of low-background technologies allowed to reach sensitivities beyond 10^{26} years of half-life, new methodological approaches and ton-scale experiments are today under study with the aim to push the sensitivity beyond the actual limit of about two orders of magnitude.[23]

In Table 2 the half-life bounds obtained in the main experiments devoted to the search for $0\nu\beta\beta$-decay are collected, in order to highlight the progress over the years.

Table 2. Results of the experiments devoted to the search for $0\nu\beta\beta$-decay.

Group and Date	Isotope	Half-Life Bound (yr)
Mateosian, Goldhaber 1966 [226]	^{48}Ca	$>2 \times 10^{20}$
Fiorini et al., 1967 [227]	^{76}Ge	$>3 \times 10^{20}$
Bardin et al., 1967 [229]	^{48}Ca	$>2 \times 10^{21}$
Fiorini et al., 1973 [228]	^{76}Ge	$>5 \times 10^{21}$
Cleveland et al., 1975 [230]	^{82}Se	$> 3.1 \times 10^{21}$
Caldwell 1989 [240]	^{76}Ge	$>1.2 \times 10^{24}$
ITEP-ErPI 1990 [241]	^{76}Ge	$>1.3 \times 10^{24}$
Heidelberg-Moscow 2001 [242]	^{76}Ge	$>1.9 \times 10^{25}$
IGEX 2002 [243]	^{76}Ge	$>1.57 \times 10^{25}$
NEMO-3 2010 [244]	^{100}Mo	$>1.1 \times 10^{24}$
CUORICINO 2011 [245]	^{130}Te	$>2.8 \times 10^{24}$

The situation is very different for the $0\nu2EC$-process, due to the strong suppression of this decay mode, characterized by a very low probability with respect to the companion $0\nu\beta\beta$-process. This happens as a result of the combination of a number of factors: a lower sensitivity of $0\nu2EC$-experiments to the absolute neutrino mass, a very low isotopic concentration of the isotopes of interest, a complicated $0\nu2EC$-effect signature and a smaller energy release. However, a resonant enhancement could take place, due to the degeneracy of the energies of the parent (A, Z) and the daughter atom $(A, Z-2)^{**}$ [218], in principle able to increase the probability up to a factor of 10^6. Despite this promising feature, there were no advancements in experimental techniques until the late 1980s, when the first high-precision mass measurements on radioactive nuclides took place [246]. More and more Penning-trap facilities were built up in the subsequent decades [247,248], leading to rapid development of the corresponding mass-measurements techniques [249,250]. As a result, mass measurements on a huge number of nuclides were carried out with a relative uncertainty of 10^{-9}, in this way boosting the search for the resonant $0\nu2EC$-process.

Currently, the highest up-to-date sensitivity to the $0\nu2EC$-process (namely 10^{21}–10^{22} yr) has been obtained by means of different experimental techniques, ranging from gaseous (^{78}Kr), scintillation (^{106}Cd) and bolometric (^{40}Ca) detectors to HPGe γ spectrometry (^{36}Ar, ^{58}Ni, ^{96}Ru, ^{112}Sn) and geochemical methods (^{130}Ba, ^{132}Ba) (see Ref. [203] and references therein). Furthermore, in the case of resonant enhancement of the $0\nu2EC$-process low-temperature bolometers look like promising candidates for a successful large-scale experiment, leading eventually to a sensitivity of the order of about 10^{25} yr [251]. Another valuable option could be to look for the $0\nu2EC$-process in radioactive nuclides with a quite long half-life and a relevant decay mode, but further challenging issues would arise: the production of large amounts of long-lived radionuclides and the realization of ultra-low background measurements in the presence of radioactive samples.

4. Conclusions

The discovery of neutrino oscillations shows that the neutrino is a massive particle, at odds with the Standard Model assumptions, but its elusive features made a determination of its absolute mass scale very challenging. As such, since the 1934 celebrated Fermi's theory of β-decay and in particular, since his proposal to infer the value of the neutrino mass from the shape of the β-spectrum in the close vicinity of the endpoint energy, further theoretical work devoted to extend and generalize Fermi's conclusions has been developed. Meanwhile, huge experimental efforts have been carried out with the aim to determine the value of the neutrino mass (or, in many cases, to put an upper limit on such a value). Neutrino oscillation experiments were found to be not sensitive to the neutrino masses but only to their mass-squared differences, so experimenters needed to gather information from different contexts. A possibility is offered by kinematics: the knowledge of the total energy of the initial state of a process involving the emission of a neutrino, for instance, a β-decay process or an orbital electron capture, and the accurate measurement of the kinematic of the final state allow to infer the determine the neutrino mass via energy and momentum conservation principle. Measurements based on kinematics are usually termed direct measurements. They are model-independent and, in particular, cannot give any information about the nature of the massive neutrino. The issue of the nature of the neutrino mass dates back to Majorana's deep intuition in 1937 and is of seminal importance. Were the massive neutrino a Majorana particle, it would provide a signature of new physics beyond the Standard Model and confirm the validity of lepton number non-conservation. As a further bonus, the leptogenesis would be accredited as the mechanism at the heart of the baryon asymmetry of the Universe. The hallmark of Majorana neutrino is the lepton number violation so a viable test of the nature of massive neutrinos would be to look for this feature in processes in which they need not be observed. A natural candidate, since Furry's proposal in 1939, is the neutrinoless double β-decay. The search for this intriguing phenomenon has been recognized to be as challenging as the measurement of the neutrino mass, because of its extremely long half-life, and also to be able to provide non-trivial information on the mass itself. Neutrinos were also predicted to be relics of the big bang within the standard cosmological model, as inferred from both measurements of the abundance of light elements and measurements of the properties of the cosmic microwave background. As such, data from cosmic surveys could be effective in providing a constraint on the sum of the neutrino masses, but this estimate is model-dependent. Another viable alternative for the determination of neutrino mass is offered by the time-of-flight measurements on neutrinos arising from very strong sources such as astrophysical events like a supernova explosion.

In this work, we retraced the long-lasting story of a paramount effort, that of measuring the mass of the most elusive particle existing in nature. We focused on direct measurements of electron neutrinos, starting from the first experimental investigation of the β-decay spectrum of a variety of isotopes and ending with the tritium, the elective choice since the beginning of the 1950s. The evolution of the experimental setups and the methodological techniques has been followed as well, ending with the most recent issues. Finally, the related crucial issue of the nature of the massive neutrino has been addressed, mainly retracing its historical origin which led to the experimental investigation of the still elusive neutrinoless double β-decay and two-electron capture phenomena.

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Abbreviations

The following abbreviations are used in this manuscript:

F-K	Fermi-Kurie
G-M	Geiger-Mueller
ITEP	Institute of Theoretical and Experimental Physics
LANL	Los Alamos National Laboratory
LNL	Livermore National Laboratories
INS	Institute of Nuclear Studies
MAC-E Filter	Magnetic Adiabatic Collimation with an Electrostatic Filter
KATRIN	Karlsruhe Tritium Neutrino
CRES	Cyclotron Radiation Emission Spectroscopy
MARE	Microcalorimeter Arrays for a Rhenium Experiment
IBEC	internal bremsstrahlung in electron capture
GUTs	grand unified theories
PMNS	Pontecorvo Maki Nakagawa Sakata
HPGe	High Purity Germanium

Notes

1 Pauli's proposal was put forward in an open letter addressed to Hans W. Geiger and Lise Meitner at a meeting in Tübingen in December 1930 [1], and later publicly expressed at the American Physical Society meeting held in Pasadena in June 1931. In fact, in 1933 at the Solvay Conference in Brussels, Pauli recalled "In June 1931, during a conference in Pasadena, I proposed the following interpretation: the conservation laws hold, the emission of beta particles occurring together with the emission of a very penetrating radiation of neutral particles, which has not been observed yet. The sum of the energies of the beta particle and the neutral particle (or the neutral particles, since one does not know whether there is one or many) emitted by the nucleus in one process, will be equal to the energy which corresponds to the upper limit of the beta spectrum" ([2], p. 324).

2 This feature followed as a result of the existing model of nuclei, consisting of protons and electrons. Indeed, according to this picture and the Ehrenfest–Oppenheimer rule [3], the ^{14}N nucleus was built of fourteen protons and seven electrons, leading to a half-integer spin and then to Fermi–Dirac statistics, at odds with experimental observations, consistent with spin-1 and Bose–Einstein statistics.

3 This critical position was shared by Niels Bohr, who had also questioned the validity of the energy conservation, in an attempt to look for a solution to the β-decay puzzle [4].

4 A corresponding penetrating power of 10^{16} km in solid matter was predicted, which led Bethe and Peierls to the pessimistic conclusion: "It is therefore absolutely impossible to observe processes of this kind with the neutrinos created in nuclear transformations" ([13], p. 532).

5 The starting point of Pontecorvo's method was the consideration that radioactive atoms produced by inverse β-ray processes and irradiated atoms have different chemical properties. Several elements can be used for neutrino irradiation, among which ^{37}Cl, and the experiment proposed by Pontecorvo is based on the following reactions: $\nu + {}^{37}\mathrm{Cl} \rightarrow e^- + {}^{37}\mathrm{Ar}$ and $^{37}\mathrm{Ar} \rightarrow {}^{37}\mathrm{Cl}$, the last one being an electron capture decay. It required the irradiation of a large volume of Chlorine or Carbon Tetra-Chloride for about one month, followed by the extraction of radioactive ^{37}Ar by boiling. Then, the radioactive isotope ^{37}Ar had to be introduced inside a small counter with a counting efficiency close to 100% [17].

6 Reines and Cowan's experiment was based on the reaction $\overline{\nu}_e + {}^1_1p \rightarrow e^+ + {}^1_0n$. According to Fermi's theory the cross section for an inverse β-decay process had to depend on the energy. As such, for antineutrinos with average energy of 3 MeV, a cross section equal to 6.3×10^{-44} cm^2 with an uncertainty of about 25 percent (due to the uncertainty of the energy spectrum of antineutrinos) was predicted. The cross section measured by Reines and Cowan was in agreement with the predicted value within 5 percent [21].

7 The muon neutrino ν_μ was detected for the first time in 1962 at Brookhaven [33].

8 The general expression is $\nu_\alpha = \sum_i U_{\alpha i}\nu_i$ where $i = 1,2,3$, $\alpha = e, \mu, \tau$ and $U_{\alpha i}$ are the elements of the Pontecorvo–Maki–Nakagawa–Sakata matrix [34,36].

9 A handful of reviews on this topic is currently available [50–53], besides the book by J. S. Allen [54]. For an up to date comprehensive account see Ref. [55].

10 Throughout this subsection and the following one the historical notation μ for the neutrino rest mass is adopted.

11 In general, the matrix element $\int v_m^* u_n d\tau$ is different from zero if the difference between the angular momentum and spin of the primary and secondary nuclei is equal to zero or one.

12 Alvarez investigated the *K*-electron capture process for several isotopes by focusing, in particular, on the transition from ^{67}Ga nucleus to the stable ^{67}Zn nucleus [80].

13 See Ref. [107] for a complete survey of the main results of the theoretical and experimental studies on the fundamental reactions involving light nuclei carried out until 1950. In particular, the endpoint energy estimates for the β-spectrum here quoted vary from (11 ± 2) keV to (18.9 ± 0.5) keV.

14 The finite resolution of spectrometers required the correction of the experimental points in order to obtain the true β-spectrum. Such a correction was shown to depend on the energy derivatives of the observed energy distribution and on the observed resolution characteristics. Ad hoc procedures were developed in order to face this problem [115,116].

15 Otherwise the absorption of low-energy electrons could introduce distortions in the measured spectra.

16 A finite neutrino mass was shown to influence essentially the region close to the endpoint of the β-spectrum [114], which led to an F-K plot turning sharply towards the energy axis. The distance between the theoretical endpoint and the endpoint obtained by the straight line extrapolation of the spectrum at low energies was equal to $\frac{\mu}{2}$ and $\frac{3\mu}{2}$ for Dirac antineutrino and neutrino, respectively, while being equal to μ in the case of a Majorana neutrino. In Ref. [114] the upper limit obtained was compatible with a Dirac neutrino picture.

17 The interesting history of the experimental efforts conducted by the ITEP group and of the general skepticism which accompanied them throughout the years is retraced in Ref. [50], pp. 196–199, to which we refer the interested reader.

18 An in depth discussion of these issues can be found in Refs. [50,53,55], to which we refer the interested reader.

19 A detailed description of the KATRIN approach and of the experimental setup is given in Refs. [52,53,74], to which we refer the interested reader.

20 A number of review articles on double β-decay and two-electron capture processes is available in the literature, to which we refer the interested reader. See for instance Refs. [197–203] and references therein.

21 This circumstance was pointed out by B. Pontecorvo in Ref. [207].

22 From its very beginning, the story of experimental searches for double β-decay has been characterized by false discoveries, which would have been superseded by subsequent attempts. A collection of these unfortunate efforts can be found in Ref. [215], to which we refer the interested reader.

23 See Refs. [238,239] for a recent and up to date review of double β-decay experiments.

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