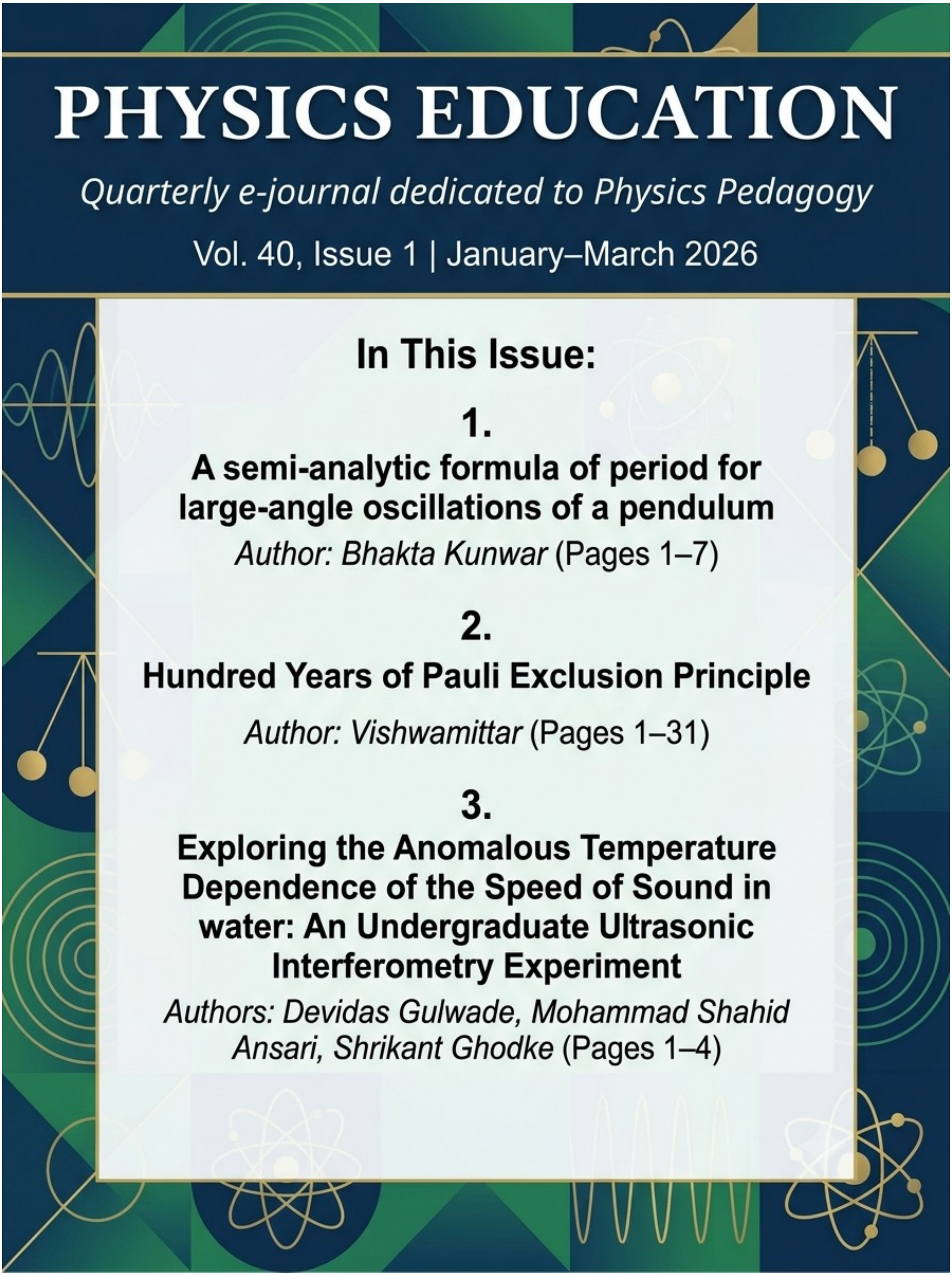

# PHYSICS EDUCATION

*Quarterly e-journal dedicated to Physics Pedagogy*

Vol. 40, Issue 1 | January–March 2026

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EDITORIAL

# Navigating the Spectrum of Physics Pedagogy: From Classical Mechanics to Quantum Milestones

Welcome to the first issue of Volume 40 of *Physics Education*. As we step into the January–March 2026 quarter, our dedication to advancing teaching methodologies and academic enrichment within higher education remains as steadfast as ever. This issue presents a carefully curated triad of papers that perfectly captures the multifaceted nature of physics instruction—spanning theoretical modeling, profound historical reflection, and hands-on laboratory investigation.

We begin this issue by revisiting a familiar cornerstone of the physics curriculum. In **"A semi-analytic formula of period for large-angle oscillations of a pendulum,"** Bhakta Kunwar expertly moves beyond the standard small-angle approximation that dominates introductory courses. By developing a semi-analytic approach, this paper provides educators with a robust, accessible mathematical tool to bridge the gap between elementary mechanics and advanced non-linear dynamics, offering a much richer classroom discussion for advanced students.

Following this, we turn our attention to a monumental landmark in modern physics. Vishwamittar's extensive review, **"Hundred Years of Pauli Exclusion Principle,"** guides readers through a century of one of the most foundational tenets of quantum mechanics. The Pauli Exclusion Principle not only shaped our understanding of atomic structure and the periodic table but also laid the groundwork for modern condensed matter physics. This comprehensive piece serves as an invaluable resource for educators seeking to infuse their lectures with deep historical context and conceptual clarity.

Finally, we ground our theoretical explorations in the essential realm of experimental practice. In **"Exploring the Anomalous Temperature Dependence of the Speed of Sound in water: An Undergraduate Ultrasonic Interferometry Experiment,"** authors Devidas Gulwade, Mohammad Shahid Ansari, and Shrikant Ghodke present a highly effective laboratory module. By investigating the unique thermal properties of water through ultrasonic interferometry, this paper exemplifies how inquiry-based experiments can be successfully integrated into the undergraduate lab to foster critical thinking and practical skill development.

Together, these contributions highlight the dynamic and evolving strategies required to effectively teach physics today. Whether you are guiding students through the intricacies of mathematical derivations, recounting the rich history of quantum discovery, or demonstrating physical phenomena in the laboratory, we hope the insights within these pages inspire and elevate your teaching practice throughout the upcoming academic year.

— **The Editorial Board**
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# A semi-analytic formula of period for large-angle oscillations of a pendulum

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## Abstract

Derivation of approximate formula for time-period of a simple pendulum for its large-angle oscillations has been carried out using polar co-ordinate $(r,\ \theta)$. The validity of the formula has been checked by comparing its results with the exact calculations obtained from elliptic integrals. An experiment was also carried out using the readily available apparatus in a general laboratory for amplitudes $\alpha \leq 80^\circ$.

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## 1 Introduction

The simple harmonic motion of a simple pendulum is introduced at high school level or at first year undergraduate level. The experiment is quite straightforward and is widely used to measure the value of acceleration due to gravity $g$ at any given place. In these experiments, students are asked to keep angular amplitudes $\alpha$ as low as possible, normally, they are asked to maintain $\alpha < 5^\circ$. The time-period $T_0$ is given by the relation $T_0 = \sqrt{l/g}$, where $l$ is the length of the pendulum. The motion of pendulum is linear for small-oscillations. But, for large-angle oscillations, the motion becomes non-linear and hence there exists no simple formula for time-period $T$ in this regime. So, students are rarely asked to perform large-amplitude oscillations.The exact value of period at different angular amplitudes can be estimated by evaluating elliptic integrals. However, the calculations are reasonably complicated for high school or first-year undergraduate students. So, it was felt by many authors that a simple linearized formula for the expression of time-period as a function of amplitude might encourage students to undertake large-amplitude experiments. Consequently, a number of such approximate formulae are available in [1, 2, 3, 4, 5, 6, 7, 8, 9] the literature. The easiest known formula for large-angle period is attributed to Bernoulli [1] and is given by $T = T_0(1+\alpha^2)/16$, where $\alpha$ is amplitude of oscillation. This formula is not suitable for a $\alpha > 40^\circ$. Onestriking formula is due to Molina [3], which yields results within 1% error for $\alpha < 112^\circ$ and it is given by $T = T_0(sin\alpha/\alpha)^{-\frac{3}{8}}$. Kidd and Fogg [4] obtained an appealing formula $T = T_0/\sqrt{cos(\alpha/2)}$, which agrees to within 1% for $\alpha < 100^\circ$ with the exact values obtained from elliptic-integrals.

There have been a host of approximate formulae dedicated to large-angle regime. Some of these include the works of Santarelli *et al.* [2], Lima and Arun [6], Beléndez *et al.* [7], Butikov [8] and Big-Alabo [9].The derivation of most of these formulae has been made through linearization/approximations/modifications. Many of these are in good agreement with the exact elliptic-integral results with their own limitations.

In the present work, we endeavor to derive a formula based on an entirely new motivation.We use the basic concepts of radial and transverse accelerations of a body moving in a plane in terms of polar co-ordinates($r$, $\theta$). But, it turned out that the formula we derived was, interestingly, the same as derived by Kidd and Fogg [4]. We hope that the present paper will give students an alternative way of scrutinizing the derivation of the formula. We have presented the discourse in a more reasonable way and it is expected to be within the reach of their pedagogical understanding.

## 2 Derivation of formula for time-period

In terms of polar co-ordinates $(r, \theta)$, radial and transverse accelerations of a body moving in a plane are given by $(\ddot{r} - r\dot{\theta}^2)\hat{r}$ and $(2\dot{r}\dot{\theta} + r\ddot{\theta})\hat{\theta}$, respectively. We take the point of suspension $O$ of the pendulum as the pole (origin) and the downward vertical straight line from the pole $O$ as the polar axis. With this orientation of the reference frame, angle $\theta$ represents instantaneous angular displacement from the equilibrium position and angle $\alpha$ represents the amplitude.

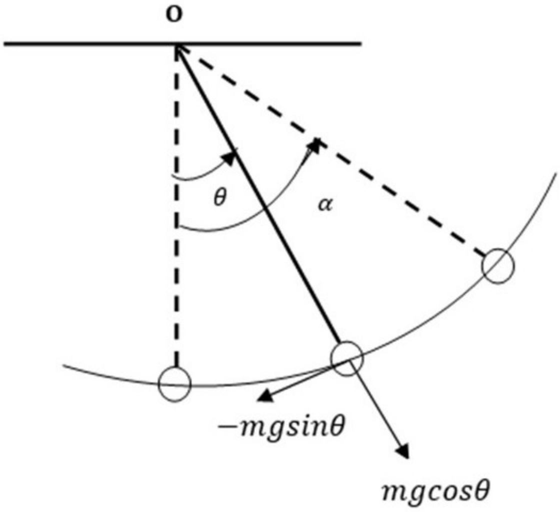

Figure 1: A schematic diagram showing the oscillation of a pendulum with amplitude $\alpha$. The dashed lines denote $\theta = 0$ and $\theta = \alpha$ positions while the solid line represent an arbitrary intermediate position.

It is evident from Fig. 1 that the tension on the string, which acts radially inward providing the necessary centripetal force, is equal to $-mgcos\theta$. Similarly, $-mgsin\theta$ is the restoring force and it acts along the tangent to the trajectory of the pendulum.

Then, the equations of motion can written as

$$m(\ddot{r} - r\dot{\theta}^2) = -mgcos\theta \tag{1}$$

$$2\dot{r}\dot{\theta} + r\ddot{\theta} = -mgsin\theta \tag{2}$$

Here, $r = l$, $\dot{r} = 0$ and $\ddot{r} = 0$. So, the above equations take the forms

$$\dot{\theta} = \sqrt{\frac{g}{l}}\sqrt{cos\theta}, \tag{3}$$

$$\ddot{\theta} = -(\frac{g}{l})sin\theta. \tag{4}$$

Eq. 4 can also be written as

$$\ddot{\theta} + \omega_0^2 sin\theta = 0, \tag{5}$$

where, $\omega_0 = \sqrt{g/l}$.

For small $\theta$, $sin\theta \approx \theta$ and Eq. (5) becomes linear and it can be expressed as $\ddot{\theta} + \omega_0^2\theta = 0$, where, $\omega_0 = \sqrt{g/l}$ is the angular frequency and $T_0 = 2\pi\sqrt{l/g}$ the time-period for small oscillations. Also, for small $\theta$, $cos\theta \approx 1$ and Eq. (3) yields $\dot{\theta} = \sqrt{\omega_0}$. Thus for small $\theta$, Eqs. (3) and (4) are consistent with each other.

For large angle oscillations, it is obvious from Eq. (3) that the instantaneous angular frequency $\dot{\theta}$ is a function of angular-displacement $\theta$ and therefore, it is natural to ask as to what should be the expression for $\dot{\theta}$ when the pendulum is oscillating with an angular-amplitude $\alpha$. The straightforward idea would be to replace the displacement $\theta$ by the amplitude $\alpha$ yielding $\dot{\theta} = \sqrt{g/l}\sqrt{cos\aleph}$. However, this would lead us to a wrong value of angular frequency as $\alpha$ is the maximum value of $\theta$ whereas it takes all the values lying between 0 and $\alpha$ during a swing. So, a simple logic to look for an appropriate replacement of $\theta$, for linearization of Eq. (3), would be to find its average value between 0 and $\alpha$, which is $\alpha/2$. With this replacement, expression for angular frequency $\omega$ in the large-amplitude regime can be obtained from Eq. (3) as $\omega = (\sqrt{g/l}\sqrt{cos(\alpha/2)})$. With $\omega_0 = \sqrt{g/l}$, the above equation takes the form $\omega = \omega_0\sqrt{cos(\alpha/2)}$, and, therefore, the time-period $T = 2\pi/\omega$ can be expressed as

$$T = \frac{T_0}{\sqrt{cos(\alpha/2)}}, \tag{6}$$

The above formula was first proposed by Kidd and Fogg [4]. However,their treatment is based on a different motivation.They obtained the force constant $k$ using the relation $k = \mid dF/ds \mid$, where the force $F = -mgsin\theta$ and the arc length $s = l\theta$. Then, one gets $k = mgcos\theta/l$ and $\omega = \sqrt{k/m} = (\sqrt{gcos\alpha/l})$ and $T = T_0/\sqrt{cos\theta}$. They evaluated the exact value of period $T_\alpha$ at large amplitude $\alpha$ using the elliptic integral

$$T_\alpha = \frac{2T_0}{\pi}\int_0^{\pi/2}\frac{d\phi}{\sqrt{1 - sin^2(\alpha/2)sin^2\phi}} \tag{7}$$

and noticed that the exact value of period $T_\alpha$ at an amplitude $\alpha$ matches well (within 1 % for $0 \leq \alpha \leq \pi/2$) when $\theta$ was replaced by $\alpha/2$ in the relation $T = T_0/\sqrt{cos\theta}$. It should be noted that Eq. (6) gives finite value of $T$ for $0 \leq \alpha < \pi$. It diverges only at amplitude $\alpha = \pi$. So, in principle, the formula should work for amplitudes much beyond 90°. But we will see later that the error rises tp 3 % at 120°.

Now, we also make an attempt to justify the use the term $\alpha/2$ in place of $\alpha$ in Eq. (6). We will see in the following section that the angular frequency $\omega$ comes naturally, with a minor linearization of a term, in the form of $\omega = \omega_0\sqrt{cos(\theta/2)}$. We use the relation $Sin\theta = 2sin(\theta/2)cos(\theta/2)$ to re-write the Eq. (4) in the form

$$\frac{\ddot{\theta}}{2} + (\frac{g}{l}cos\frac{\theta}{2})sin\frac{\theta}{2} = 0. \tag{8}$$

we can write Eq. (8) in the form

$$\frac{\ddot{\theta}}{2} + \omega^2 sin\frac{\theta}{2} = 0, \tag{9}$$

where $\omega^2 = (g/l)cos(\theta/2)$.

Eq. (9) is similar to Eq. (5) except for two facts. Firstly, the instantaneous displacement in Eq. (5) is $\theta$ while that in Eq. (9) is $\theta/2$. Secondly, the term $\omega^2$ in Eq. (9) is not a constant but a variable and is dependent on displacement $\theta$. If we replace the variable displacement $\theta$ by the constant amplitude $\alpha$, then, $\omega^2$ becomes a constant. Denoting this constant value of $\omega^2$ by $\omega^{2_\alpha}$, we can write

$$\omega_\alpha^2 = \frac{g}{l}cos\frac{\alpha}{2}. \tag{10}$$

With this minor but rational modification, Eq. (9) can be written as

$$\frac{\ddot{\theta}}{2} + \omega_\alpha^2 sin\frac{\theta}{2} = 0. \tag{11}$$

In the small-angle regime, $sin(\theta/2) \approx \theta/2$, then Eq. (11) can be expressed as

$$\ddot{\theta} + \omega_0^2\theta = 0, \tag{12}$$

which clearly represents a linear harmonic oscillation with angular frequency $\omega_\alpha$ and time-period $T = T_0/\sqrt{cos(\alpha/2)}$ which is same as Eq.(6). The derivations from Eq. (8) to (12), based on the trigonometric formula $2sin(\theta/2)cos(\theta/2)$, was carried out after a long deliberation. However, while searching the literature later, it was found that the formula $ain\theta = 2sin(\theta/2)cos(\theta/2)$ was employed by the author L. E. Millet [5] in explaining the use of the term $\alpha/2$ instead of $\alpha$ in Eq. (6), but their reasoning and treatment is slightly different from ours.

We computed both $T$ from Eq. (6) and $T_\alpha$ from Eq. (7) and compared them for the range of amplitudes $0° \leq \alpha < 180°$ for evaluation of the exact period $T_\alpha$ we run a simple fortran code implementing Simpson's 1/3 rule for numerical integration. A good agreement was observed between the two over a wide range of amplitudes as can be seen from Fig. 2, where we have plotted the values of $T$ and $T_\alpha$ as a functional amplitude $\alpha$ taking $T_0 = 1$. The difference between the two results is less than 0.001 % for

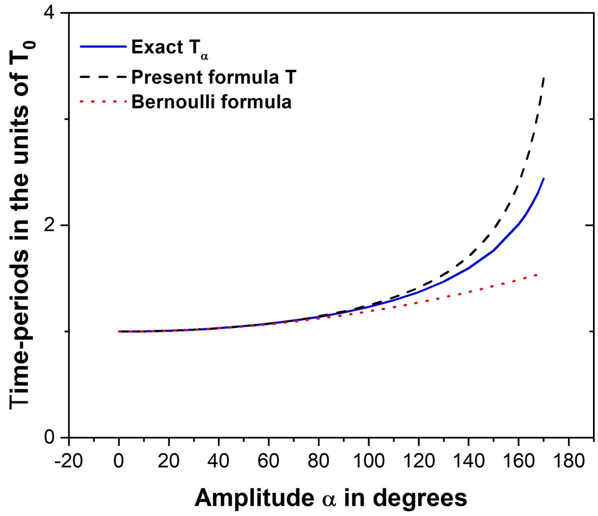

Figure 2: Curves showing variation of time-period (in the units of $T_0$) with angular amplitudes. The solid line in blue color represents the exact period $T_\alpha$, the dotted line in red color represents the approximate period due to Bernoulli [1] and the dashed line in black color represents period $T$ calculated from our formula of Eq. (6).

$\alpha \leq 20°$, it becomes 0.751 % at 90°, 3.011 % at 120°, about 10 % at 147°. However, the difference rises rapidly beyond 150° and it becomes as high as 174.4 % at 179°. It is also observed that the approximate period $T$ is always higher than the exact period $T_\alpha$.

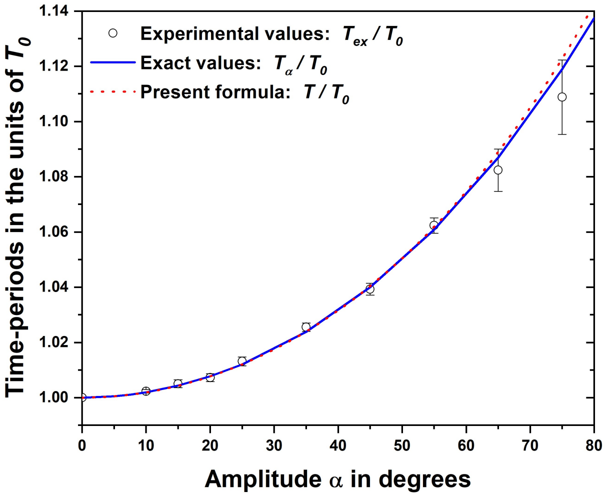

Figure 3: Curves showing variation of time-period (in the units of $T_0$) with amplitudes. The solid line in blue color represents the ratio $T_\alpha / T_0$, where $T_\alpha$ is the exact period obtained from elliptic-integrals. The dashed line in red color represents the ratio $T/T_0$, where $T$ is the period calculated from the present formula of Eq. (6) and the circles denote ratio of experimental data, $T_{ex}/T_0$.

## 3 Experiment

We performed an experiment with the readily available apparatus, namely a spherical-brass-bob of diameter 2.3 cm and an inextensible thread. Friction at the point of suspension was reduced by using two interlocked brass-rings having toroidal shapes. The experiments were carried out at a place having altitude $h = 350$ m from mean sea level. We calculated the value of acceleration due to gravity g at this place using the relation $g = g_0(1+h/R_e)^{(}-2)$. Taking $g_0 = 9.8ms^{(}-2)$ and $R_e = 6378$ km, we obtained $g = 9.7989ms^{(}-2)$. The effective length l of the pendulum was 166.9 cm. We calculated the small-angle period $T_0$ using the relation $T_0 = 2\pi\sqrt{l/g}$ and found $T_0 = 2.5931$ s. Experimentally measured value of $T_0$ was found to be $2.5930 \pm 0.0004$ s and it is the weighted mean of several observations, we recorded up to 280 swings in one of the observations. The error in period for each observation was taken as $(0.2/N)$ s where $N$ is total number of swings in that observation. The excellent agreement between the calculated and the measured value of $T_0$ showed that the pendulum was working within tolerable limits of air damping and friction at the peg.

It is well known that, at large-angle oscillations, one can get only few swings owing to large air damping. We could observe about 85 swings at angles between 5° and 10°, about 20 swings between 20° and 30° and only about 3 swings between 70° and 80°. So, it becomes difficult for human eyes to make precise measurements at higher angles. Therefore, we limited our observations at angles below 90°. The measurement at each amplitude is actually obtained by including the swings within a small range of amplitudes centered around that amplitude. For example, measurement at 35° is obtained by recording the time taken by all the possible number of swings between 30° and 40° The experimentally measured period $T_{ex}$ at large amplitudes have been presented in Table 1. The values of $T_{ex}/T_0$, $T_\alpha/T_0$ and $T/T_0$ are also presented in the table. The entries within brackets in the third row of Table 1 represent errors in the measurement of the ratios $T_{ex}/T_0$. The experimental results have also been depicted graphically in Fig. 3.

Table 1: Measured values of time-period $T_{ex}$ and the ratios $T_{ex}/T_0$, $T_\alpha/T_0$ and $T/T_0$ at different angular amplitudes. The figures within brackets in the third row represent errors in the measurement of the ratio $T_{ex}/T_0$.

| Angles in degrees | 10° | 15° | 20° | 25° | 35° | 45° | 55° | 65° | 75° |
|---|---|---|---|---|---|---|---|---|---|
| Period $T_{ex}$ in s | 2.5989<br>±0.0016 | 2.6060<br>±0.0036 | 2.6118<br>±0.0037 | 2.6270<br>±0.0042 | 2.6591<br>±0.0039 | 2.6948<br>±0.0056 | 2.7547<br>±0.0072 | 2.8065<br>±0.0200 | 2.8752<br>±0.0348 |
| $T_{ex}/T_0$ | 1.00229<br>(0.00061) | 1.00503<br>(0.00138) | 1.00725<br>(0.00143) | 1.01313<br>(0.00161) | 1.02549<br>(0.00149) | 1.03927<br>(0.00215) | 1.06235<br>(0.00279) | 1.08234<br>(0.00771) | 1.10881<br>(0.01243) |
| $T_\alpha/T_0$ | 1.00191 | 1.00430 | 1.00767 | 1.001203 | 1.02383 | 1.03997 | 1.06083 | 1.08692 | 1.11896 |
| $T/T_0$ | 1.00191 | 1.00431 | 1.00768 | 1.01207 | 1.02398 | 1.04038 | 1.06178 | 1.08889 | 1.12271 |

## 4 Conclusion

We derived a formula for time-period $T = T_0/\sqrt{cos(\alpha/2)}$ for large-angle oscillations of a simple pendulum. The formula was first derived by Kidd and Fogg [4] following a different line of motivation.The derivation is lucid and graspableby first year college students. The reason for the introduction of the term $\alpha/2$ in place of $\alpha$ has been elucidated qualitatively as well as analytically. The difference between our result and the exact value is negligible at smaller angles and it increases to 0.24 % (1.2 %) at 70° (100°). The difference rises to 10 % at 147°.We have also illustrated the possibility to carry out experiments to measure periods at amplitudes $\alpha \leq 80^\circ$ with ordinary apparatus in a high school laboratory. For comparing such results the formula is sufficient. In fact, the experimental error occurring in an ordinary simple experiment, where times are recorded manually, would be higher than the difference between the exactperiod $T_\alpha$ and the approximate period $T$ for $\alpha \leq 60^\circ$.

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# Hundred Years of Pauli Exclusion Principle

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* *The article is dedicated with immense gratitude and profound regards to my affectionate sisters late Smt. Krishna Ji, late Smt. Nirmal Ji, Smt. Prem Ji, Smt. Amrit Ji, and Sudarshan Ji, and their families, and with deep reverence to my respected late maan Ji (Smt. Lachhmi Devi Ji).*

## Abstract

Guided by his extraordinary intellectual spark, in January 1925 Pauli hypothesized that in an atom there cannot be two or more electrons with the same set of values for their four quantum numbers. Soon this axiom became a fundamental cornerstone of quantum mechanics, whose early two formalisms were published in the second half of 1925 and the first half of 1926. Then, it was generalized as a principle to restrict the simultaneous occupancy of a quantum state in a system by two or more identical half-integer spin particles, which are described by wavefunctions antisymmetric under interchange of two particles. This article is devoted to a comprehensive description of theoretical aspects of this principle, its multifarious applications in physics, chemistry, materials science, and astrophysics. Also included are an assortment of some relevant remarks and a biosketch of Pauli.

**Keywords:** Pauli exclusion principle, Symmetric and antisymmetric wavefunctions, Exchange force, Structure of atoms and the periodic table, Nuclear shell model, Crystal binding, Electron-positron theory, White dwarf and neutron stars, Wolfgang Pauli.

## 1. Introduction

Spectroscopy, which studies the interaction of matter with electromagnetic radiation, was initially developed for visible light and used as a tool for thumbprinting chemical elements because of their unique spectral signature, leading to the discovery of many new ones and the study of astronomical objects. As time passed, a wide range of electromagnetic spectrum became explorable and the scope of applications of spectroscopy was enhanced opening a new era (studies going beyond emission and absorption spectra of atoms and molecules to include blackbody radiation and even the spectroscopy of nuclei).

Theoretical interpretation of various accurate findings in spectroscopy together with the results of some other experiments painstakingly performed over the years played a vital role first in the creation of the old quantum theory and then that of the new quantum mechanics (QM) which has successfully elucidated the structure and properties of atoms, molecules, materials, and even nuclei. Interestingly, Bohr's model in old quantum theory, and Heisenberg's matrix-based formalism and Schrödinger's wave equation in QM were all tested by describing hydrogen spectra. In fact, this process has continued as the development of a variety of modern technology-based spectroscopic techniques has yielded extremely precise experimental data, which, in turn, has led to a better understanding of things at quantum scales – spectroscopy, the mother of QM still goes on nurturing it.

The failure of the prevalent concepts of old quantum theory to explain the experimentally observed fine structure in the spectral lines of many elements and the anomalous patterns recorded in the Zeeman spectra of a few elements led Pauli (December 1924) to assert that the electrons have an intrinsic characteristic non-classical two-valued property. Also, influenced by his findings on the classification of spectral terms in a strong magnetic field, in a research paper submitted for publication on January 16, 1925, to *Zeitschrift für Physik*, Pauli put forth the following precept (see p. 2 in [1]). *'In an atom there cannot be two or more equivalent electrons, for which in strong fields the values of all the four quantum numbers coincide. If an electron exists in an atom for which these numbers have definite values, then this state is occupied'.* Here, the four quantum numbers considered by him were the energy-specifying quantum number ($n$), the orbital angular momentum quantum number ($l$), two-valued property based new quantum number $l \pm 1/2$, and projection of $l \pm 1/2$. He did not give any interpretation of the new quantum number (and its projection) as he believed this to be a non-classical entity, which had values $\pm 1/2$ for $l = 0$.

The ultimate recognition of the two-valued property of electrons as their intrinsic angular momentum spin having discrete value $\hbar/2 = 5.273 \times 10^{-35}$ Js (reduced Planck's constant times spin quantum number $s = 1/2$) finally led to identification of the last two quantum numbers as total angular momentum quantum number for a single electron in an atom $j = l \pm 1/2$, and its projection $m_j$ along the axis of quantization defined by an applied magnetic field. $m_j$ is called the magnetic total quantum number and can have values $-j, -j+1, \ldots, j-1, j$. It may be pointed out that discreteness of the value of spin implied that the magnetic moment of the electrons associated with their intrinsic angular momentum also has a two-valued quantum nature.

It must be emphasized that the concept of (quantized) spin has no classical equivalent, is properly understood using relativistic QM or quantum field theory and is incorporated in non-relativistic QM phenomenologically by including it as an additional degree of freedom in the Hamiltonian and the wavefunctions of the system to take care of the physical effect under consideration. In the framework of QM, the state of an electron in an atom can be completely defined not only by the four quantum numbers $n, l, j, m_j$ but also by $n, l, m_l, m_s$; $n$ is called the principal or total quantum number. Here, like $m_j$, $m_l$ and $m_s$ are the projections of $l$ and $s$ along the axis of quantization defined by an applied magnetic field and are known as magnetic orbital quantum number and magnetic spin quantum number, respectively. These can have values $m_l = 0, \pm 1, \ldots, \pm l - 1, \pm l$ and $m_s = \pm 1/2$; $m_s = 1/2$ and $-1/2$ are usually referred to as up (↑) and down (↓) spins indicating the orientation of a hypothetical vector representing the spin. In view of the remarks made here, Pauli's proposal could be reformulated as following: *In any multielectron atom, no two electrons can have simultaneously the same values for a set of the defining quantum numbers* $n, l, j, m_j$ *or* $n, l, m_l, m_s$.

In due course, the assertion 'excluding the possibility of two electrons occupying the same quantum state (defined by the four quantum numbers) in an atom' was extended to other many-electron systems, incorporated in the newly created QM and christened as the Pauli exclusion principle (PEP). Also, the enunciation of PEP was followed by the discovery of this being a consequence of antisymmetry property of many electron wavefunctions with respect to interchange of two of these, independently by Heisenberg and Dirac in mid-1926. Thus, these two publications provided a QM based justification for the PEP. In his paper, Dirac also derived the distribution function and some statistical quantities for assemblies of noninteracting entities described by antisymmetric and symmetric wavefunctions (under exchange of these entities). The results for the two cases differed significantly and those for the latter were the same as had been obtained by Bose for the quanta of light (photons) and by Einstein for the particles in 1924 and 1925, respectively. Note that the entities considered by them were not subjected to any PEP type restriction.

In 1926, and prior to Dirac's work, Fermi proved that physical systems in thermodynamic equilibrium containing molecules satisfying PEP would be governed by the statistical formulae different from those determined by Bose and Einstein. Interestingly, his results agreed with those found by Dirac for the assembly of particles described by antisymmetric wavefunctions. These two kinds of statistics are known as Bose-Einstein and Fermi-Dirac statistics, and the particles following these are classified as bosons and fermions, respectively. Obviously, these publications highlighting the connection between PEP and nature of statistics obeyed, clearly enlarged the scope of PEP beyond multielectron atoms.

Furthermore, as more and more elementary particles were discovered in the subsequent years, it was experimentally shown that the elucidation of particles with half-integer spin quantum number $s = 1/2, 3/2, \ldots$ requires antisymmetric wavefunctions while those having zero or integral spin $s = 0, 1, 2, \ldots$ are described by symmetric wavefunctions. Thus, it was established that half-integer spin particles are fermions and zero or integer spin particles are bosons. This is known as spin-statistics connection. Some examples of the former category of particles with $s = 1/2$ for which PEP holds good are electrons, protons, neutrons, neutrinos, etc., while photons ($s = 1$), pions ($s = 0$), kaons ($s = 0$), etc. belong to the latter category which is not governed by PEP.

In the meantime, Ehrenfest and Oppenheimer (1931) proved that a composite system or a cluster of electrons and protons followed PEP if the number of its constituent particles was odd yielding a half-integer spin of the collection; for an even number of constituents the total spin was an integer number, and it did not obey PEP. In view of these facts, PEP can be generalized to read: *two or more identical half-integer spin particles (fermions), which are described by wavefunctions antisymmetric under interchange of two particles, can never be in the same quantum state at any one time.*

It may be mentioned that atomic nuclei as well as atoms are typical examples of stable composite systems comprising spin half fermions – protons, neutrons (collectively called nucleons because of their role in the atomic nucleus), and electrons. Thus, nuclei having odd number of nucleons and atoms containing odd number of nucleons plus electrons are fermions while those having even value for these numbers are bosons. As such, helium-3 nuclei (comprising 3 nucleons) and lithium-6 atoms (having 6 nucleons and 3 electrons) are fermions, while helium-4 nuclei or alpha particles (containing 4 nucleons) and lithium-7 atoms (having 7 nucleons and 3 electrons), are bosons. It may be added that the pions involved as exchange particles mediating nucleon-nucleon short-range strong forces in the nuclei have zero spin and their number does not change the situation arising from the total number of aggregate half-integer spin nucleons. Also, atoms constitute electrically uncharged fermions and bosons depending on the total number of nucleons and electrons in them.

In his work, Pauli used the PEP to get the correct atomic numbers 2, 8, 18, 32, …for the lengths of the periods in the periodic table of elements and thus got answer to a problem with which he had been wrestling since 1922. Also, Pauli, Bohr and co-workers used this principle to develop the models of all atoms from hydrogen to uranium, explained the periodic changes of atomic volumes and ionization potentials, and accounted for the valencies, chemical affinities, and many other properties of the atoms. The first formal application of PEP in the form of Fermi-Dirac statistics was made in 1926 by Fowler to discuss astrophysical problem of thermodynamic equilibrium of white dwarf stars. Remarkably, this work brought out a wonderful fusion of QM and gravitation.

The purpose of this article is to commemorate 100 years of enunciation of PEP by presenting a comprehensive pedagogical review of this fascinating topic. This introductory account [1,4] is followed by a thorough discussion of theoretical aspects of PEP [2,3] in Section 2, while in Section 3 we delve into its varied glorious applications [2-7] in different branches of science. Some pertinent comments [8-15] constitute the content of Section 4, and the article is concluded in Section 5 [16,17]. As a tribute to the rare inherent capabilities of its propounder, we have given a brief account of Pauli's life and his marvelous professional contributions [1,7, 18-22] in Appendices 1-4.

## 2. Exchange of Indistinguishable Particles, Antisymmetric Wavefunctions and PEP [2,3]

In QM, the phrase 'identical particles' is used to signify not only the same value of intrinsic physical properties like rest mass, electric charge, spin, magnetic moment, etc., for these but also complete indistinguishability implying that the particles cannot be labelled or earmarked so that we cannot identify them on being interchanged or after colliding with each other. Thus, identical nature of quantum particles implies that in a system if two of these are interchanged then there is no effect on any of the associated physical quantities and hence there is no physical means to distinguish the two situations. This aspect is fully supported by the experimental findings such as: (i) the spectra of a particular atom, say sodium, (ii) the decay products of a specific nucleus, say $^{242}$Cm, and (iii) particular elementary particles, say muons observed in cosmic rays, and so on, are always the same irrespective of the laboratory where these studies are carried out. Had these entities or their constituents been distinguishable then experiments performed at different places would have yielded observably different results. Obviously, indistinguishability of quantum particles has no classical counterpart.

Now, complete description of the physical state of a quantum system requires knowledge of its wavefunction determined by all its degrees of freedom (spatial coordinates as well as spin) or set of quantum numbers including spin for the electrons in an atom, and time if the system is not stationary. Generally, the wavefunction including the spin is called a total wavefunction. Thus, considering the system at a particular time or assuming this to be stationary, interchange of two identical quantum particles comprises not only the exchange of spatial coordinates or quantum numbers but also of the spin labels. Accordingly, the fact that interchange of two identical quantum particles does not lead to any observable change in their configuration (and hence any difference in the associated physical quantities) implies that relevant probability density is not affected by the exchange of spatial coordinates or the quantum numbers, and the spin labels of the pair under consideration.

Thus, if the total wavefunction of a quantum system of identical particles in a particular situation, is denoted by $\psi$ then new wavefunction $\psi'$ obtained on interchanging a pair of these particles in it will be such that $|\psi'|^2 = |\psi|^2$. This implies that

$$\psi' = \pm\psi. \tag{1}$$

Therefore, the mathematical form of the wavefunctions is such that on interchange of two particles it either remains the same or changes sign. The wavefunctions pertaining to these two situations are said to be symmetric and antisymmetric, respectively, and are generally denoted by $\psi_S$ and $\psi_A$. The inference that the wavefunction for identical particles must be either symmetric or antisymmetric is usually referred to as the indistinguishability principle. Also, it is found that the symmetric or antisymmetric nature of a wavefunction does not change with time, i.e., if a state is symmetric or antisymmetric at any time, it will always be so. Thus, $\psi_S$ and $\psi_A$ have definite exchange symmetry.

To make things clearer, we consider a two-particle system using 1 and 2 for the two particles (assuming that these can be labelled) and denoting specific one-particle states (determined by the relevant spatial coordinates and spin or the set of quantum numbers) by $a$ and $b$. The corresponding wavefunctions $\psi_a$ and $\psi_b$ are product of a spatial part and a spin part when the relevant coordinates are independent. Ignoring all interactions between these particles, we can write the two-particle wavefunction as the product of the two one-particle states yielding the following two possibilities:

$$\psi_{ab}(1,2) = \psi_a(1)\psi_b(2) \tag{2}$$

and

$$\psi_{ba}(1,2) = \psi_b(1)\psi_a(2). \tag{3}$$

The most general normalized two-particle wavefunction will be a linear combination of the two states defined in Eqs. (2)-(3):

$$\psi_\pm = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2)]. \tag{4}$$

Introducing a linear particle exchange operator $\hat{P}_{12}$ that interchanges particles 1 and 2 in the system, we have

$$\hat{P}_{12}\psi_\pm = \frac{1}{\sqrt{2}}[\hat{P}_{12}\psi_a(1)\psi_b(2) \pm \hat{P}_{12}\psi_b(1)\psi_a(2)]$$

$$\begin{aligned} &= \frac{1}{\sqrt{2}}[\psi_a(2)\psi_b(1) \pm \psi_b(2)\psi_a(1)] \\ &= \frac{1}{\sqrt{2}}[\pm\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)] \\ &= \pm\frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2)] \\ &= \pm\psi_\pm. \end{aligned} \quad (5)$$

Also,

$$\begin{aligned} \hat{P}_{21}\psi_\pm &= \frac{1}{\sqrt{2}}[\hat{P}_{21}\psi_a(1)\psi_b(2) \pm \hat{P}_{21}\psi_b(1)\psi_a(2)] \\ &= \frac{1}{\sqrt{2}}[\psi_a(2)\psi_b(1) \pm \psi_b(2)\psi_a(1)], \end{aligned} \quad (6)$$

which, in view of the second line in Eq. (5) gives $\hat{P}_{21}\psi_\pm = \hat{P}_{12}\psi_\pm$ and, hence, $\hat{P}_{21} = \hat{P}_{12}$. These considerations show that the interchange of two particles changes sign of $\psi_-$ but not of $\psi_+$ so that the latter is a symmetric function while the former is an antisymmetric function. Thus, we have

$$\psi_S \equiv \psi_+ = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)] \quad (7)$$

and

$$\psi_A \equiv \psi_- = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)] \quad (8)$$

for a two-particle system. It is pertinent to note that if the preceding interchange of particles is repeated then we get the original situation implying that $\hat{P}_{12}^2 = 1$.

Now, assuming the two particles to be in the same quantum state (violating the PEP), we replace subscript $b$ by $a$, and get

$$\begin{aligned} \psi_S &= \frac{1}{\sqrt{2}}[\psi_a(1)\psi_a(2) + \psi_a(1)\psi_a(2)] \\ &= \sqrt{2}\psi_a(1)\psi_a(2) = \sqrt{2}\psi_{aa}(1,2) \end{aligned} \quad (9)$$

and

$$\psi_A = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2)] = 0. \quad (10)$$

Obviously, $\psi_A$ rules out the possibility of the two particles being in the same quantum state implying that PEP is automatically satisfied by the two-particle system described by the antisymmetric wavefunction. This corroborates what has been said in Section 1, wherein it has also been mentioned that the particles described by antisymmetric wavefunctions are fermions. Accordingly, we can say that Eq. (8) defines wavefunction for a system comprising two noninteracting identical fermions.

Note that Eq. (8) can also be written as a 2 × 2 determinant,

$$\psi_A = \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix}. \quad (11)$$

Here, we have replaced the normalization factor $1/\sqrt{2}$ by $1/\sqrt{2!}$, reason for which will be clear shortly. As an extension of this, wavefunction for a system of three noninteracting identical fermions, which is antisymmetric for the interchange of any pair of these, can be expressed as a 3 × 3 determinant

$$\psi_A = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_a(1) & \psi_a(2) & \psi_a(3) \\ \psi_b(1) & \psi_b(2) & \psi_b(3) \\ \psi_c(1) & \psi_c(2) & \psi_c(3) \end{vmatrix}, \quad (12)$$

with $1/\sqrt{3!}$ as normalization factor. Generalizing these, for a system of $N$ identical fermions, the wavefunction which is antisymmetric for the interchange of any pair of these, will be a $N \times N$ determinant with $1/\sqrt{N!}$ as normalization factor. Note that interchange of two particles means interchange of two rows and hence a change in sign taking care of antisymmetry. Also, if two fermions are in the same quantum state then subscripts for two rows of the determinant will be the same and the determinant will vanish leading to zero probability of occurrence of such a situation. Thus, expressing the fermion wavefunction as a determinant is not only a compact form for writing this, but it also affirms its antisymmetric nature and ensures that PEP is followed. It may be added that such a determinantal representation of $N$ particle total wavefunctions is usually referred to as Slater determinant.

As pointed out earlier, interchange of a pair of identical particles can be implemented by exchanging their spatial coordinates or three quantum numbers for electrons in the atoms, and the spin labels. Since the elementary particles constituting the classically known matter are fermions with spin $1/2$, we confine the remaining discussion in this section to this case.

For a system of two identical particles, if the potential energy does not depend on spin labels, its Hamiltonian and, hence, the wavefunction associated with the spatial coordinates or quantum numbers, will be completely symmetric under interchange of the particles. Asymmetry of the wavefunction can arise only from the contribution of the two possible values $+1/2$ and $-1/2$ of the spin label which lead to two different spin states. If we assume both the particles to be in the same spin state (say, $+1/2$), then this together with the same spatial coordinates or corresponding quantum numbers for electrons in an atom makes subscript $b$ the same as subscript $a$ in Eq. (11) leading to $\psi_A = 0$ in accord with PEP. On the other hand, for the case of two fermions in two different spin states ($+1/2$ and $-1/2$), $\psi_A$ is nonzero despite the same values of spatial coordinates or corresponding quantum numbers. Thus, even two noninteracting identical fermions have a tendency of being away or mutual repulsion when their spins are in the same state (parallel spins ↑↑) and to be together or attract each other when their spins are opposite (antiparallel spins ↑↓). It may be added that parallel (↑↑) or antiparallel (↑↓) spins of a pair of a particular kind of fermions result in their total spin $S$ as 1 or 0, respectively. Since $S = 1$ can have components $-1, 0$, and 1, it is called a triplet state, while $S = 0$ with only one component is a singlet state. This unique force leading to avoidance (in the triplet state) or togetherness (in the singlet state) of two identical fermions, having its origin in the antisymmetry of wavefunction under interchange of indistinguishable particles, is known as exchange force. Note that it is not really a force because no physical agency pushes the particles and is purely quantum mechanical in nature with no classical counterpart. The tendency of the same spin state identical fermions to stay away to satisfy PEP is called

Pauli repulsion. It will be nonzero only when the two wavefunctions overlap, indicating quantum mechanical interaction between the particles. Obviously, the strength of this repulsion will be determined by the extent of overlap of the relevant wavefunctions, and it will be absent for the fermions separated by a large distance.

Before proceeding further, it may be mentioned that the concept of exchange operation introduced for two identical particles above can be easily extended to a many-particle system described by a $N$-particle total wavefunction. Here, an interchange of a pair of particles identified by the labels $i$ and $j$ is brought about by the exchange operator $\hat{P}_{ij}$, which is found to be such that $\hat{P}_{ji} = \hat{P}_{ij}$ and $\hat{P}_{ij}^2 = 1$. $\hat{P}_{ij}$ is also called permutation operator. Furthermore, the states of a $N$-particle system are described by either totally symmetric ($\psi_S$) or totally antisymmetric ($\psi_A$) wavefunctions.

When many fermions are confined in a finite region, these will occupy the needed number of energy states from the lowest upwards as necessitated by PEP. Since these particles are distributed over the quantum states with nonzero energy values, these have finite internal energy (and hence kinetic energy) which implies the existence of an outward (kinetic) pressure. Obviously, this pressure is of quantum mechanical origin and has nothing to do with the Coulombic interaction of the fermions. It exists even at 0 K and will be quite substantial if the number density of particles is large.

## 3. Some Applications of PEP

### i. Structure of Atoms and the Periodic Table [2,4]

If the coupling of electron spin with the orbital angular momentum and other consequent interactions are ignored then the state of an electron in an atom is uniquely defined by the four quantum numbers $n, l, m_l, m_s$. The principal or total quantum number $n (= 1, 2, 3, \ldots)$ and the orbital quantum number $l (= 0, 1, 2, \ldots, n-1)$ define a shell and a subshell, respectively. The magnetic orbital quantum number $m_l (= 0, \pm 1, \ldots, \pm l)$, and magnetic spin quantum number $m_s (= \pm 1/2)$ govern the fine structure of the energy shells and distribution of the electrons in these. Based on the early spectroscopic nomenclature, it is conventional to denote the $l = 0, 1, 2, 3$ values by $s, p, d, f$ referring to the first letter of spectral groups sharp, principal, diffuse, and fundamental; sequential alphabets $g, h, \ldots$ are used for $l = 4, 5, \ldots$. From the allowed values of $l$ and the fact that $l \leq n-1$, it is clear that $n = 1$ shell will have only one subshell, called $1s$; the $n = 2$ shell will have two subshells $2s$ and $2p$; the $n = 3$ shell will have subshells $3s, 3p$, and $3d$; and so on. Usually, an electron state is written as $n$ followed by the letter for the corresponding $l$ value and the number of electrons in the subshell is indicated by a superscript after this letter. Thus, $3d^9$ represents an electronic state defined by $n = 3$, $l = 2$ and having 9 electrons in the subshell. Note that all the electrons in a subshell have the same values of $n$ and $l$.

According to PEP, no two electrons in an atom can have the same set of values of $n, l, m_l$, and $m_s$ so that two electrons characterized by $m_s = 1/2$ and $-1/2$ can have identical values of quantum numbers $n, l$, and $m_l$. A specific set of values of these three quantum numbers defines an orbital in the atom. Thus, an orbital can accommodate at most two electrons with opposite spins ($m_s = 1/2$ and $-1/2$) and these are said to be paired. On the other hand, the word unpaired refers to the situation that the orbital is occupied by a single electron having $m_s = 1/2$ or $-1/2$. Now, for a particular value of $l$ there are $2l + 1$ allowed values of $m_l$ and each of these can have two electrons with opposite spins so that a subshell defined by quantum number $l$ can at most accommodate $2(2l + 1)$ electrons. Thus, the $s, p, d, f, \ldots$ subshells can hold 2, 6, 10, 14, ... electrons, respectively. Now, since $l$ itself can assume $n$ values from 0 to $n - 1$, the total number of electrons in a shell with quantum number $n$ can be

$$\sum_{l=0}^{n-1} 2(2l+1) = 2\left[2\sum_{l=0}^{n-1} l + n\right]$$
$$= 2[n(n-1) + n] = 2n^2.$$

Accordingly, the shells identified by $n = 1, 2, 3, 4, \ldots$ can accommodate 2, 8, 18, 32, ... electrons at most. The completely filled shells in an atom have paired electrons and are called the closed shells. On the other hand, the outermost unfilled shell can have paired or unpaired electrons and is known as the valence shell. The electrons in the valence shell participate in bonding and hence the degree of occupancy of this shell and the extent of bonding of the electrons to the atom determine many aspects of the chemical and physical properties of the substances obtained from these. The atoms having unpaired electrons in the valence shell are chemically highly active as these try to pair up with other electrons having opposite spin. In contrast, elements with closed outermost shells are chemically inactive and extremely stable.

Now, if we consider a neutral atom with atomic number $Z$, then in the ground state the $Z$ electrons will occupy the lowest possible energy states in accord with the PEP. The distribution of electrons in different shells and subshells of an atom is known as its electron configuration. Thus, for a hydrogen atom ($Z = 1$), only $n = 1$ shell is occupied for which allowed value of $l$ is 0 implying $m_l = 0$ and electronic state is expressed as $1s^1$; the electron can have spin state $m_s = 1/2$ or $-1/2$. In helium ($Z = 2$), both the electrons occupy $n = 1$ shell and have $l = 0, m_l = 0$ but will have opposite spins; its electron configuration reads $1s^2$. Since $n = 1$ shell can accommodate at most 2 electrons, the shell of helium atom is closed, while it is unfilled in the hydrogen atom with one valence electron. In the case of lithium ($Z = 3$), first two electrons go to the $n = 1$ shell and $l = 0$ subshell (spin states $1/2$ and $-1/2$), while the third electron must occupy $n = 2$ shell and $l = 0$

subshell. Accordingly, electron configuration for lithium reads $1s^22s^1$. Similarly, the electron configuration for beryllium ($Z = 4$) is $1s^22s^2$ (opposite spin electrons in the $2s$ subshell) and for boron ($Z = 5$) it is $1s^22s^22p^1$. Continuing in this way, we reach neon ($Z = 10$) which has electron configuration $1s^22s^22p^6$ implying that $n = 2$ shell is filled and then $n = 3$ shell will begin to start being populated, and so on. The presence of unpaired electrons in the valence shells of H, Li, and boron makes these highly active compared to beryllium which has paired electrons in the outermost subshell. Furthermore, helium and neon are inert because their outermost shells are closed.

The periodic table is obtained by building up of atoms by adding more and more electrons to the appropriately selected nucleus. The same number of electrons in the outermost shells, corresponding to different $n$ values, accounts for the periodicity in the behaviour of the elements. However, there are some exceptions to the above-illustrated orderly filling of shells and subshells. For example, in the case of $Z = 21$ to 28 elements, the $4s$ subshell is filled before the $3d$ subshell because the former has slightly lower energy than the latter. Thus, $3d$ subshell is the valence shell for these elements. As a typical example of this, note that electron configuration of iron ($Z = 26$) is $1s^22s^22p^63s^23p^63d^64s^2$, where $3d$ subshell is still short of its maximum occupancy of 10 by 4 while the subshell $4s$ has been filled. These deviations from the anticipated ordering for building up of atoms and different departures observed in the arrangement of atoms in the periodic table (such as, the third period has 8 elements with $n = 3$ rather than expected 18 elements as found in the preceding paragraph) have their origin in a combination of many subtle effects, which become more and more important for large values of $Z$ and their discussion is beyond the scope of the present article.

### ii. Atomic Magnetism

The restriction of the electron (or fermion) spin to up and down situations implies that the associated intrinsic magnetic moment too can have only two corresponding orientations in space. Thus, magnetic moments of two paired electrons with opposite spins (as required by PEP) will cancel each other so that only atoms having unpaired electrons in their valence shell will have a non-zero spin associated magnetic moment. The vector combination of this magnetic moment with the net magnetic moment arising from the orbital motion of the electrons gives the total magnetic moment of the atom as the contribution of the nuclear magnetic moments is thousands of times smaller.

### iii. Nuclear Shell Model [2,4]

The nucleus of an atom with atomic number $Z$ and mass number $A$ has $Z$ protons and $N = A - Z$ neutrons bound together by a strong nuclear force. As mentioned in Section 1, protons and neutrons together are called nucleons so that $A$ is also the nucleon number. The concept of the nuclear shell structure was put forth mainly to account for the periodic variation in their many properties. In this model, each nucleon is assumed to be moving under the influence of an average potential field of all the other nucleons. The nuclear force is not only short-range but also spin dependent which leads to coupling of the spin of each nucleon to its own orbital angular momentum, whose nature is different for the light and the heavy nuclei.

The quantum state of a nucleon in the nuclear energy levels is also represented by four quantum numbers (though somewhat different from those mentioned in (i) above) and the shells and subshells are identified by the same labels as in the case of atoms. The filling of the nuclear energy states by the nucleons is also compatible with PEP. Since protons and neutrons are distinct fermions two each of these with opposite spins can occupy the $1s$ nuclear state and so on. It is found that nuclear shells are completely filled in respect of protons or neutrons when the number of a particular kind of nucleon is one of the following: 2, 8, 20, 28, 50, 82, and 126. These numbers are called magic numbers as the nuclei containing this number of protons or neutrons are more stable (and hence abundant), have unusually large number of isotopes (atoms of a chemical element with the same $Z$ value but different $A$), and exhibit some other typically different nuclear properties. These aspects become more prominent if the number of protons as well as the neutrons is a magic number. Such nuclei are said to be doubly magic. Helium ($Z = 2$), oxygen ($Z = 8$), tin ($Z = 50$), and lead ($Z = 82$) are typical magic number nuclei. Helium-4 ($Z = N = 2$), oxygen-16 ($Z = N = 8$), lead-208 ($Z = 82, N = 126$) are highly stable doubly magic nuclei. Tin ($Z = 50$) has 10 stable isotopes, while its neighbouring elements indium ($Z = 49$) and antimony ($Z = 51$) have only two isotopes each.

### iv. Molecule Formation [3]

A molecule is a group of two or more atoms that form the smallest identifiable unit with a definite structure held together by the chemical bonds formed by the valence electrons of its constituents. In fact, when two or more atoms are brought close, their electronic wavefunctions overlap so that PEP comes into play and the consequent chemical bond is formed in accord with this principle. The idea that only valence electrons participate in the chemical bonding is corroborated by the x-ray spectroscopy. The quantum states of the resulting aggregates are called molecular orbitals. The creation of bonds in the molecules generally involves unpaired electrons and is dictated by their quantum states and the way these are shared and arranged in the aggregate. The compliance of these aspects with PEP brings out the importance of this principle in the formation of molecules. When two unpaired electrons with opposite spins belonging to different atoms form a chemical bond, these become paired, and any other unpaired electron will combine with another unpaired electron to form a different bond.

We illustrate the possibility of formation of molecules by considering the following simple cases of diatomic molecules. An aggregate of two hydrogen atoms involves unpaired 1$s$ electrons from the two participating atoms yielding a stable hydrogen molecule ($H_2$) having two opposite spin electrons in its molecular orbital. However, a triatomic hydrogen molecule ($H_3$) cannot exist as it will require the presence of three electrons in the 1$s$ state. In the case of helium atom, the outermost orbit is closed with paired electrons and there is no possibility of bond formation leading to a diatomic helium molecule. Lithium with electron configuration $1s^2 2s^1$ has an unpaired 2$s$ electron so that it can form a diatomic molecule ($Li_2$) with paired electrons in the outermost molecular orbital. However, the absence of any unpaired electron in the valence orbit of beryllium atom ($1s^2 2s^2$) rules out the possibility of the existence of its diatomic molecule. In contrast, an unpaired 2$p$ electron in boron implies the existence of its diatomic molecule ($B_2$).

## v. Ortho and Para Hydrogen [2,6]

The formation of a $H_2$ molecule involves two atoms with distinct nuclei containing one proton each. Accordingly, PEP does not impose any restriction on the spins of the participating protons, and these can have parallel ($\uparrow\uparrow$) or antiparallel ($\uparrow\downarrow$) spins leading to total nuclear spin $S$ for the molecule as 1 or 0, respectively. Thus, we can have the triplet and the singlet nuclear states for this molecule. The molecules comprising triplet state nuclei are referred to as ortho hydrogen and those having singlet state nuclei are called parahydrogen. These two forms are sometimes called nuclear spin isomers. It is important to note that the ortho and para forms differ in their physical properties but not in the chemical properties which are determined by their electron configuration and not the nuclear spin states. Assuming the same statistical weight for all the nuclear states, in a sample of hydrogen gas in thermal equilibrium the number of ortho $H_2$ molecules should be thrice that of para $H_2$ molecules. This indeed is so as is evident from the following experiments.

a. In the rotational infra-red spectra of hydrogen gas at ordinary temperatures, the bands corresponding to the transitions allowed in the ortho hydrogen are nearly three times more intense than those pertaining to the para hydrogen.

b. The experimental data for the constant volume specific heat of hydrogen between 20 K and 250 K (where only the rotational motion contributes) is in nice agreement with the weighted mean of the two theoretically calculated specific heat values for the two forms. It may be mentioned that ortho-para behaviour is not the prerogative of hydrogen only, it is observed in many other molecules also.

### vi. Fermion Statistics [5,6]

It has been mentioned in Section 1 that a collection of the noninteracting particles in thermodynamic equilibrium obeying PEP, i.e., the fermions is governed by the Fermi-Dirac statistics where the distribution function is distinctly different from that for the collection of the bosons. Therefore, the general behaviour shown by the systems following the Fermi-Dirac statistics will be different from that of the collection of the bosons. Because of the restriction that not more than two fermions can occupy a quantum state, we can never have a situation where a large number of fermions accumulate in a single energy state. So, these particles cannot show a phenomenon like Bose-Einstein condensation. Furthermore, the energy density of a collection of fermions is larger than that for the same number of bosons. As such, the systems where Fermi-Dirac statistics is used constitute examples of the application of PEP. To mention a few, we can list magnetic behaviour of an ideal Fermi gas, thermionic and photoelectric emission of electrons from metals, Thomas-Fermi statistical model of atom, and calculation of virial coefficients for low density real Fermi systems.

### vii. Crystal Binding [5]

A usual solid crystal is a three-dimensional arrangement of a very large number of atoms or group of atoms in a periodic structure of lattice and can be obtained by bringing together its constituents. When these isolated atoms are brought closer, the wavefunctions or the charge distributions in their shells and subshells gradually overlap and the electrons belonging to one atom are likely to occupy in part the quantum states of another atom and vice versa. This tendency and the extent of occupancy of the interatomic states are governed by PEP and lead to bonding in the crystal. Also, equilibrium crystal structure is determined by the optimum use of space for the participating atoms and the condition that the total interaction energy, including Coulombic repulsion between the nuclei, is minimum. This aspect is also influenced by the PEP because the final configuration should also comply with this principle.

In the ionic crystals, one or more electrons from one atom are transferred to another to achieve a stable closed shell electron configuration for both. The former category of atoms becomes positively charged ions (cations) while the latter are negatively charged ions (anions) and the Coulombic attraction between these is responsible for the (ionic) bonding which is quite strong. The electrostatic repulsion between similar charges rules out the possibility of the identical ions being nearest neighbours in the crystal. Thus, each cation is surrounded by an appropriate number of anions and vice versa. As an example of this bonding, we consider the case of sodium chloride. Here, sodium atom (Na, $Z = 11$) with electron configuration $1s^22s^22p^63s^1$ loses the outermost $3s^1$ electron to the chlorine atom (Cl, $Z = 17$) having configuration $1s^22s^22p^63s^23p^5$ yielding closed shell structures for the singly charged ions $Na^+$ and $Cl^-$.

If the bond is formed by two electrons having opposite spins (as per requirement of the PEP) and shared one each by the participating atoms to attain a closed shell structure, then it is called a covalent bond. The binding in silicon (Si, $Z = 14, 1s^22s^22p^63s^23p^2$) crystals is a typical example of this category, where each atom shares its four valence electrons with its four nearest neighbours to attain the closed shell configuration $1s^22s^22p^63s^23p^6$ in each case.

It may be remarked that in the ionic bonding the electrons are concentrated around the participating atoms, while in the covalent bonding these pile up between the atoms. Also, the two bondings are not only reasonably strong but are also the extreme cases. In majority of crystals, generally, the bonding is a mixture of these two because the positively charged cation distorts the electron wavefunction of the neighbouring anion leading to a partial sharing of electrons fulfilling the PEP and presence of covalent bond. Even sodium chloride, though primarily an ionic compound, does have some covalent character.

It is interesting to note that the inert gases except helium form simple crystals with close packing. Here, since the outermost atomic shells are already filled, PEP prohibits any exchange of electrons. However, the charge distribution in the outermost closed shells gets slightly distorted due to small overlap of the wavefunctions of the electrons belonging to the atoms being brought close and this, in turn, induces dipole moments in these atoms which leads to a reasonably weak attractive interaction, the so-called van der Waals bonding. Further overlap of the wavefunctions is opposed by the PEP - caused repulsion because the shells are fully occupied.

### viii. Electronic Band Structure of Solids [5]

As mentioned in (vii) above, a solid crystal is formed by bringing together a very large number ($N$) of isolated atoms. This process leads to an overlap of the electron shells and subshells creating an extremely large number of levels (determined by $N$) spaced within a quite small energy width so that these can be considered as a continuum of the allowed energy values for the electronic states in the bulk crystal - the so-called energy bands. The allowed energy bands are generally separated by forbidden energy regions which are devoid of the electron energy states. These are usually referred to as energy gaps or band gaps. The bands corresponding to the inner closed shells of the atoms are known as core bands. The band pertaining to the valence electrons is called valence band and the one above this with a forbidden energy gap (having characteristic value) in between is referred to as the conduction band; in the metals the valence and conduction bands overlap. The distribution of the (atomic) electrons in the energy bands is governed by PEP. The $2N$ electrons which originally occupied the collective $1s$ state of the isolated atoms fill the $1s$ band. Similarly, the $2s$ and the $2p$ bands will have $2N$ and $6N$ electrons in them, respectively. The same logic is followed for filling the higher energy bands such that at 0 K the electrons occupy the lowest energy states available to them. It may be added that every solid has its own characteristic energy band structure, which is responsible for its electrical, optical and thermal properties. Thus, the band structure model very well accounts for the distinction between metals, semimetals, semiconductors, and insulators.

### ix. Exchange Interaction and Magnetic Behaviour [2,3,5,6]

Substances which have net magnetic moment (spontaneous magnetization) below a characteristic critical temperature even in the absence of an applied magnetic field are known as magnetic materials. Ferromagnetic and ferrimagnetic materials belong to this category. From a variety of experimental and theoretical studies, it has been concluded that ferromagnetism can be attributed to electron spins ($\pm 1/2$) localized at the lattice sites. Now consider two such entities at the sites labelled as $i$ and $j$. These electrons will interact through repulsive Coulombic force and PEP induced exchange force discussed in the last but second paragraph of Section 2. It is conventional to write the total interaction energy of these two electrons as $K_{ij} \pm J_{ij}$, where $K_{ij}$ and $J_{ij}$ are direct or Coulomb energy integral and exchange energy integral, respectively. These are determined using the relevant interaction potential and the wave functions of the two electrons; $J_{ij}$ (having its origin in PEP) depends on the degree of overlap of the wavefunctions involved. Here, upper sign corresponds to the opposite or antiparallel spins $\uparrow\downarrow$ while the lower sign to the same or parallel spins $\uparrow\uparrow$. In fact, it is found that the relative orientation of spins affects the overlap of the two electron wave functions and, hence, their $K_{ij}$ value also, which is always positive. The difference in the energy of the spin states $\uparrow\uparrow$ (triplet) and $\uparrow\downarrow$ (singlet), given by $\epsilon_{\uparrow\uparrow} - \epsilon_{\uparrow\downarrow} = -2J_{ij}$, is known as exchange energy or exchange splitting. Obviously, it is the energy required to flip the spin of a particular electron. If $J_{ij} > 0$, then the state $\uparrow\uparrow$ is more stable than the state $\uparrow\downarrow$ and such a system exhibits ferromagnetism. On the other hand, if $J_{ij} < 0$, the state $\uparrow\downarrow$ becomes favoured over the state $\uparrow\uparrow$ so that the nearest neighbouring atoms have opposite spins and we get antiferromagnetic behaviour. However, the latter type of materials do not have spontaneous magnetization because the antiparallel arrangement of equal spins makes net magnetic moment zero even below the relevant critical temperature.

Generally, the value of $J_{ij}$ decreases sufficiently fast as the separation of the two spins is increased implying that these interactions are essentially short ranged. Accordingly, while developing theoretical models for magnetic materials we consider only the nearest neighbor spin pairs and replace $J_{ij}$ by a common constant $J$.

It may be mentioned that in the ferrimagnetic compounds, the contributing ions have unequal spins and ordering at some lattice sites partially cancels the effect of the ordering at the other sites resulting in a nonzero but relatively small net magnetic moment. Their systematic theoretical description involves nearest neighbour exchange integrals corresponding to different pairs of sites. Also, the arrangement of spins in a material as parallel or antiparallel is opposed by their thermal agitation, and at higher temperatures (greater than the critical temperature) the randomization destroys the spin order and, hence, spontaneous magnetization. Furthermore, explanation given here for the three types of magnetism is quite simplified and band structure models containing both collective and localized aspects are needed for their proper description.

### x. Exchange Interaction and the Excited States of Helium and Other Multielectron Atoms [2]

The concept of Coulomb energy and exchange energy integrals with the same sign convention as in (ix), is also used in the description of the excited states of helium and other multielectron atoms. Here, the subscripts $i$ and $j$ identifying the lattice sites in (ix) are replaced by those pertaining to the relevant atomic wavefunction. It is found that the exchange integral (arising from requirements of PEP) plays an important role in determining the energy levels of excited states, particularly the singlet and the triplet electronic states. Also, like the Coulomb integral, the exchange integral for atoms is always positive. Consequently, the exchange interaction increases the energy of the singlet state and decreases that of the triplet state.

### xi. Nanostructures

Materials having at least one dimension in the range 1 and 100 nanometers are called nanomaterials. Carbon nanotubes and quantum wires having nanoscale restriction in two dimensions, and metal nanoparticles and quantum dots with all the three dimensions in nano range are typical examples of these. This restriction on one or more spatial dimensions of solids seriously affects their structure, surface area to volume ratio, bonding, band structure, and even the arrangement of discrete energy states. These make quantum effects more important and adherence to PEP in the distribution of electrons in the available energy states and bands becomes more crucial. This dramatically changes their physical, electrical, magnetic, and optical properties, that can be monitored by controlling their size and shape.

### xii. Cooper Pairs [5]

The phenomenon of sudden drop of the electrical resistivity of numerous metals, many alloys, and some chemical compounds to zero and complete expulsion of the magnetic flux from the material at a temperature lower than a characteristic critical temperature is called superconductivity. Its quantum mechanical theory, which successfully explains the experimental observations, is based on the concept of Cooper pairs. According to this theory, as a negatively charged electron passes through a solid its Coulombic interaction with the positively charged ion cores disturbs their distribution in the lattice leading to a slightly higher concentration of positive charges along the trajectory. However, this deformation and its reversal are reasonably slow because the ion cores are much heavier than the electrons. Another electron moving through this polarized region of the ion lattice will then be attracted towards it because of increased charge density. Thus, the second electron indirectly interacts with the first electron via the deformed lattice resulting in a weak attractive force. If this attractive electron-lattice-electron interaction is stronger than the electron-electron Coulombic repulsion, then these two electrons couple to form a bound entity – the Cooper pair. To avoid their PEP – associated quantum mechanical repulsion, the two participating electrons must have opposite spins so that a Cooper pair is a boson with zero spin. The binding energy of the Cooper pair is $\sim 10^{-3}$ eV. This accounts for the low value of the critical temperature; at this temperature, the Cooper pair dissociates, and superconductivity disappears. The detailed theory, which makes an explicit use of PEP for the wavefunction of the two electrons, shows that the two electrons constituting a Cooper pair are moving in opposite directions and that the continuously changing separation of the electrons defines size of the Cooper pair, which is $\sim 10^{-6}$ m. This aspect justifies the zero electric current. Furthermore, the high density of the Cooper pairs (bosons) in the ground state and their collective behaviour explains the macroscopic effects associated with superconductivity. It may be added that the Cooper pairs mechanism alone cannot explain the phenomenon of superconductivity in the chemical compounds, which have relatively higher values of the critical temperature.

### xiii. Dirac's Electron-Positron Theory [4]

While developing the quantum description of electrons having relativistic energies, Dirac (1928, 1930) very elegantly fused together quantum mechanics and special relativity. On the one hand, his equation accounted for the origin of electron spin and its magnetic moment in a natural way and on the other it predicted the existence of both positive $\geq m_e c^2$ and negative $\leq -m_e c^2$ energy states for the free electron. Here, $m_e$ is electron mass and $c$ is the speed of light in vacuum. Obviously, the former corresponded to positive inertial mass while the latter to negative inertial mass. Rather than ignoring the negative energy states as a mathematical artifact and still to be consistent with the common observation of electrons having positive energies, he resolved this paradoxical situation by postulating that all the negative energy states pertaining to the negative mass were uniformly filled in accord with the PEP (two electrons with opposite spin in each energy level). Electrons in the filled negative energy states are said to form 'Dirac sea' or 'Dirac ocean'. Obviously, there is an energy gap of $2m_ec^2$ ($= 1.02$ MeV) between the highest filled negative energy state and the lowest positive energy state. Since there is no vacancy in the Dirac sea, the PEP prohibits (a) dropping of an electron from the positive energy states into the fully occupied Dirac sea, and (b) transition of an electron within this sea under the influence of an external force and, hence, ruling out the possibility of its direct observation with any kind of physical measuring devices. However, if an electron in the Dirac sea is excited to a positive energy state by supplying an energy (say by absorbing a photon) $\geq 2m_ec^2$, a hole is created there leading to a shortage of negative energy, negative charge and negative mass. The latter two will be equivalent to positive charge and positive mass so that the hole would respond to an external force as an entity with a positive electric charge and the same (positive) mass and spin as electron, and can, thus, be observed. The hole (exact mirror image of the electron) has been identified as an antiparticle of electron and named positron, and it was experimentally observed in the cosmic rays by Anderson in 1932. It may be added that positrons are also produced in the decay of proton-rich radioactive nuclei like oxygen ($A = 15$) and fluorine ($A = 18$). It is also worth mentioning that the preceding interpretation about creation of positron as a hole in the Dirac sea has got support from the fact that the positron and the electron are produced together in pair production experiments carried out in the laboratory using high energy accelerators.

Note that if a vacancy or hole is created in the negative energy states then an electron can fall into this hole (in compliance with PEP) emitting an energy $\geq 1.02$ MeV (in the form of $\gamma$-radiation) leading to simultaneous disappearance of an electron and a positron. This complete conversion of masses of both into energy is called electron-positron annihilation. Practically, this process takes place whenever an electron and a positron come sufficiently close. The electron-positron annihilation forms the basis of positron emission tomography and positron annihilation spectroscopy. The former is used as a diagnostic technique by creating three-dimensional images of the biochemical changes taking place in the human body. The latter finds application as a non-destructive technique to study variations in density, voids and defects in solids.

It may be pointed out that the idea of

Dirac sea becomes unnecessary in the framework of quantum field theory where the concept of antiparticles is taken care of naturally and that all elementary particles have their antiparticles; photon, and neutral particles pion and eta being their own antiparticles.

### xiv. Statistical Equilibrium of White Dwarf and Neutron Stars [6,7]

White dwarf stars are reasonably old white but faint stars having mass comparable to that of the sun ($\sim 2 \times 10^{30}$ kg) and volume comparable to that of the earth ($\sim 10^{21}$ m$^3$). These stars have almost exhausted their hydrogen content so that the energy producing thermonuclear reactions are very slow making them faint. Helium ($Z = 2$, mass $= 6.6 \times 10^{-27}$ kg) is the main constituent of these stars, whose first and second ionization energies are 24.6 eV and 54.4 eV, respectively. The gas in this star is completely ionized because the mean thermal energy per particle ($\sim 10^3$ eV) corresponding to its core temperature ($\sim 10^7$ K) is much larger than the two ionization energies of the helium atom. Therefore, a white dwarf star contains $N(\sim 10^{56})$ helium nuclei and $2N$ electrons. Since a helium nucleus is nearly 7300 times heavier than an electron, in the first approximation it can be assumed that only the electrons contribute to the dynamics of the system. Furthermore, on an average, the inter-electron Coulombic repulsion is almost balanced by the attractive force of the helium nuclei, these electrons can be treated as a noninteracting gas. Thus, a white dwarf star can be considered as a massive spherical ball comprising a very dense core of bare helium nuclei surrounded by the ideal electron gas of number density $\sim 10^{35}$ m$^{-3}$. The distribution of these electrons in the energy states in this ball is controlled by PEP and these follow the Fermi-Dirac statistics. As pointed out in the last paragraph of Section 2, these electrons produce an outward pressure which counterbalances the inward large gravitational force of the closely packed helium nuclei and, thus, leads to a thermodynamic equilibrium against the gravitational collapse of these stars. However, a star will continue to shrink to form a neutron star or a black hole if the inward gravitational force is stronger than the outward electron gas pressure. It may be added that in a rigorous theory of these stars, developed by Chandrasekhar, it was found that the outward pressure stemming from PEP can prevent gravitational collapse only if mass of the star is less than a limiting value of about 1.44 times the solar mass. This is called the Chandrasekhar limit.

Neutron stars, which are remnants of massive stars, are the second smallest and densest known class of astronomical objects having density of $3.7 - 5.9 \times 10^{17}$ kg m$^{-3}$. These are believed to be composed of mainly neutrons and, once created, they do not undergo any heat forming activity. Neutrons being fermions, occupy extremely close energy levels in accord with the PEP and are governed by the Fermi-Dirac statistics. In the simple model of neutron stars, the outward pressure arising from the distribution of the confined neutrons in the energy states is assumed to counteract the inward large gravitational force of the exceedingly closely packed neutrons with number density $\sim 10^{44}$ m$^{-3}$, which checks further collapse of the star into a black hole. However, proper description of these stars involves consideration of general relativity and repulsive nuclear forces.

## Miscellany

**(i).** During the last many years, Kaplan (see [8] for a detailed discussion) has analyzed the problem of theoretical basis of PEP using the concept of permutation symmetry group. It has been shown that (a) the simple argument leading to the fact that the wavefunction for identical particles must be either totally symmetric or antisymmetric under interchange of two of these (Eq. (1)), corresponds to one-dimensional irreducible representation of the permutation group, and (b) one cannot get any information about the permutation symmetry of the wavefunction in the multidimensional representation. It has also been found that compatibility of the permutation symmetry with the concept of independence of identical particles demands that only symmetric and antisymmetric permutation states can exist in nature. This, in turn, rules out the possibility of discovery of elementary particles that are neither fermions nor bosons, making these two the universal categories. However, it may be mentioned that anyons, which exhibit exotic statistical behaviour common to both fermions and bosons and are highly resistant to external disturbances, have been predicted to exist only in two-dimensional and one-dimensional structures and not in the real-world three-dimensional systems. As such, these have been experimentally observed as quasiparticles in the two-dimensional arrangements like the fractional quantum Hall effect systems, superconducting circuits, and graphene. Also, very recently, direct experimental evidence for their occurrence in the one-dimensional quantum systems has been reported for ultracold rubidium atoms arranged in a line using a laser standing wave.

Note that, in view of the fact that spin quantum number $s$ is zero or an integer for bosons and half-integer for fermions, Eq. (1) can be written as $\psi' = (-1)^{2s}\psi = e^{i\pi 2s}\psi = e^{i\alpha\pi}\psi$, where $\alpha = 2s$. Obviously, $e^{i\alpha\pi}$ can be taken as the phase factor introduced by the exchange of two noninteracting identical bosons or fermions. Thus, $\alpha = 0$ for bosons like pions and kaons, while $\alpha = 1$ for most of the fermions (electrons, protons, neutrons, muons, neutrinos, etc). The situation $0 < \alpha < 1$ corresponds to the case of anyons, which substantiates the fact that these quasiparticles are governed by fractional statistics.

**(ii).** From the discussion in Section 2, it is clear that PEP prevents a pair of identical fermions with same spin from being close to each other but favours the pair having opposite spins to occupy the same quantum state. Thus, this principle provides some kind of quantum mechanism that produces correlation between position of these particles. In other words, compliance of a pair of identical fermions with PEP makes them correlated or entangled, which is essentially a curious quantum property of compound systems. In 2007, Cavalcanti et al [9] systematically analyzed this aspect and developed a scheme to create entanglement using semiconductor quantum wells. The PEP is used to make the spins of two independent electrons in the conduction band entangled. Selective electron-hole recombination then makes this entanglement to appear as a specific polarization of emitted photons, which can eventually be used as a resource for different quantum information protocols. Also, recently, Hackl et al (2023) [10] have proposed an experiment in a multi-quantum-dot system that can produce highly entangled fermionic states which can be ultimately used for quantum information processing as well as quantum computer architectures.

**(iii).** Pauli repulsion between the same spin state identical fermions at short distance, discussed in the last but second paragraph of Section 2, is equally possible in atomic nuclei which are composite systems of nucleons. Accordingly, efforts have been made to include its effect in the nucleus-nucleus potential while formulating models for some nuclear reactions. In one such case, it has been shown that this phenomenon plays an important role in heavy-ion fusion at deep sub-barrier energies and provides a natural (though insufficient) explanation for the experimentally observed deep sub-barrier fusion hindrance [11].

**(iv).** The elaboration of atoms using PEP in Section 3 justifies why (a) various atoms have unique electron configuration and their aggregates have different physical and chemical properties, and (b) atoms and, hence, bulk matter (which is composed of a large number of nuclei and electrons) has volume, and no substance can be compressed beyond a limiting small region. It is worth mentioning that a rigorous theory for stability of bulk matter (a basic enigma of classical physics) using some inequalities was given in 1967-68, and its improved version was put forth in 1975. This is called Dyson-Lenard-Lieb-Thirring theory for stability of matter and involves PEP as a crucial ingredient. One of the main inferences of this theory is that any material object described by only mutual Coulombic interactions would collapse into a minuscule volume and PEP induced repulsion is essential to make it stable [7].

**(v).** Description of the stochastic processes pertaining to time evolution of fermionic systems under the influence of noise must take care of the constraints imposed by the PEP as it prohibits transfer of the particles to a quantum state that is already occupied. Accordingly, appropriate theoretical models have been developed for various such processes including the fermion Brownian motion [6].

**(vi).** Unique crystal-like geometric structures of charge-neutral non-interacting fermions formed in a strong trapping potential solely by the coaction of kinetic energy and the PEP have been named Pauli crystals. These are thus simple manifestations of Fermi-Dirac statistics in confined geometries, and their shape is determined by an interplay between the symmetry of the potential and the inter-particle correlations present in a particular many-body quantum state. It has also been shown theoretically and through numerical simulations that interactions mediated by light can improve this quantum crystallization. These crystals have recently (2021) been observed using a few ultra-cold spin-polarized fermionic $^6$Li atoms confined to a symmetric two-dimensional harmonic trap [12].

**(vii).** Quantum information theory is a fast-evolving field that unifies the principles of QM and the information theory with the aim to use quantum systems for information processing, storage, and transmission. Qubits are the fundamental units of quantum information similar to classical bits in traditional computing and are, thus, the building blocks of quantum computers. These are generally based on fermionic systems like electrons in atoms or quantum dots. This makes use of the PEP essential for their operation. Besides, the algorithms for quantum computing that rely on the manipulation of fermionic systems must comply with the restrictions associated with the PEP.

**(viii).** Dependence of the electric charge tunneling characteristics of weakly coupled quantum dot systems on the spin states of electrons in the two dots and consequent current rectification under proper biasing conditions is known as spin blockade. This was first reported in 2002 [13], is attributed to impediment caused by the alignment of spins in both the dots and is, thus, a direct manifestation of PEP. This so-called Pauli spin blockade is quite important in qubit manipulation and read out, and, hence, in quantum computing. So far, this phenomenon has been observed at low temperatures, but recent research work (2025) has shown the possibility of its existence at room temperatures. This will, in turn, help in the development of some room temperature quantum technologies [14].

**(ix).** Based on the support from outcome of the experimental and computational studies, the exceptionally long life of peptide bonds in collagen, which is found even in the bones of many million years old fossils, has been recently (2024) attributed to the role of PEP in a specific electronic interaction which protects these bonds against hydrolysis [15].

## Epilogue

Influenced by the fact that the fundamental laws like parity conservation and charge-parity invariance could be violated, theoretical models for small possible violation of PEP were suggested in 1987. Soon experimental work was started in this direction and since then a variety of pioneering experiments has been performed by many workers (see [1,16] for their discussion). These extremely precise experiments have been meticulously designed to search for (a) the PEP-violating unusual stable atoms or nuclei, (b) the PEP forbidden or non-Paulian atomic X-ray transitions involving the filled $1s^2$ level in different elements, and (c) the PEP prohibited nuclear transitions pertaining to emission of $\gamma$-rays, protons, neutrons, and $\beta$-rays. The probability of possible breach has been found to be less than $10^{-17}$ for (a), $10^{-26}$ for (b), and $10^{-35}$ for a specific nucleus in (c). In addition to these experiments, a simulation experiment performed with many-fermion quantum states randomly prepared on a quantum computer, and published in 2019 [17], confirmed the validity of the generalized PEP with an error of 1 part in $10^{18}$. Obviously, all these findings rule out the possibility of violation of this principle. On the other hand, the results of application of the PEP to various quantum phenomena and systems have been found to be fully endorsed by the relevant experiments. Accordingly, we close this article with the statement '*the PEP is a doubtless bedrock of QM with many diverse and far-reaching practical uses in physics, chemistry, materials science, astrophysics, and in the design of qubits as well as the development of algorithms in quantum computing*'.

# Appendix 1: An Overview of Great Moments in the life of Wolfgang Ernst Friedrich Pauli [7, 18-22]

The phenomenal theoretical physicist Pauli, a genius among geniuses, was born in an eminent erudite family in Vienna (Austria) on April 25, 1900 and was brought up in a very conducive-to-learning environment. During schooling in his hometown, he developed a great command on mathematics and physics and graduated from Döblinger Gymnasium in July 1918 with distinction. After this, he joined the University of Munich (Germany) where he completed his Ph D degree on the topic 'About the model of the hydrogen molecular ion' in July 1921 under the supervision of brilliant physicist Sommerfeld, who had a very high opinion about the research reported in the thesis because of its substantial mathematical rigor. However, Pauli himself was not happy with his work as its theoretical predictions were at variance with the available experimental data. In fact, this was due to the limitations of the old quantum theory on which the formulation was based.

Then, from October 1921 to 1923, he

worked as research assistant to Born (Göttingen University, Germany), Wilhelm Lenz (University of Hamburg, Germany), and Bohr (Institute for Theoretical Physics, Copenhagen, Denmark). These assignments were followed by his appointment as privatdozent at the University of Hamburg from 1923 to 1928, and then in April 1928 as professor at ETH Zurich (Switzerland) where he spent most of his life except visiting professorships at some American universities including the Institute for Advanced Study, Princeton, where he stayed during the World War II from 1940 to 1946. He became a naturalized citizen of USA in 1946 but decided to return to Zurich after the World War and got Swiss citizenship in 1949. He died of pancreatic cancer on December 15, 1958, at Zurich.

Unfortunately, Pauli's mother, to whom he was extremely close, committed suicide in November 1927 and his marriage solemnized in December 1929 with Käthe Deppner ended in a divorce in less than a year. These two mishappenings and some other developments in the family had a turmoilous psychological effect on him that led him to heavy drinking, erratic nightlife, and ultimately to severe depression in 1931-32 bringing out lack of his emotional security. Therefore, he consulted the renowned psychiatrist Jung (a professor at the University of Zurich, who analysed significantly large number of Pauli's dreams) and was under his treatment only for a short period. Eventually both became good friends and long-time research-collaborators. He went for a second marriage with Franziska Bertram in April 1934 and, luckily, she proved to be a source of great strength to him.

Pauli was awarded the 1945 Nobel Prize for physics 'for the discovery of exclusion principle' [18]. Obviously, this recognition came quite late as compared to the other cerebral giants involved in the captivating and thrilling creation of QM (see, Appendix 2 for his key contributions). Besides, he was honoured with Lorentz Medal (1931), Franklin Medal (1952), Foreign membership of the Royal Society (1953), presidentship of the Swiss Physical Society (1955), Max Planck Medal (1958), and many other prestigious awards.

## Appendix 2: A Historical Capsule of Pauli's Research Accomplishments [1, 18-22]

Pauli's research contributions started quite early. He submitted his first paper on theory of general relativity (which he learnt on his own) within two months of passing out from the Gymnasium so that his debut as physicist was in his teens at an age of about 18 years. This was followed by two more papers on the same topic soon after joining the university at Munich. These three papers on general relativity were highly admired by the great mathematician Weyl though in the third paper he had criticized some of Weyl's ideas. Then came an old quantum theory-based paper on magnetic properties of matter in mid-1920, in which he gave the name Bohr magneton to the magnetic moment of an electron associated with its orbital angular momentum. Also, recognizing his intellectual capabilities and impressed by his depth of understanding of the theory of relativity, in 1920 Sommerfeld asked him to write a review article on this topic for the *Encyclopedia of Mathematical Sciences*. This superb article of 237 pages and having 394 footnotes was submitted in 1921, two months after the completion of his Ph D degree. This was profoundly praised by Einstein for its clarity of comprehension, appropriate coverage of literature, systematic and cogent development of the subject, physical insight, and critical appraisal. This thorough and incisive work on special and general relativities brought him into limelight at such a young age. In 1949, in the article 'Some Reminiscences of My Teaching Career' (published in Amer. J. Phys., Vol 17, pp. 315-16, 1949), Sommerfeld wrote, "I suggested to Pauli that we write an article on the theory of relativity for the Mathematischen Encyclopädie together. But when he showed me the first draft of his essay, it proved to be so masterly that I renounced all collaboration. The work of the 22-year-old is unsurpassed to date."

Pauli's association with Born and Bohr and later frequent stays at Copenhagen made him a major player in the great revolution of science – the quantum mechanics (QM) and its philosophical foundation. He is remembered not only for his outstanding innovative research but also for his meticulously written letters (which sometimes were more than 10 pages long) containing marvellous new ideas, thought provoking remarks, and even derivations and critical perceptive comments on others' work, which were sometimes even harsh. In fact, his contributions of this type could have resulted in independent or co-authored publications, but he never bothered about credit for his work because for him collective effort in decoding the book of nature was more important. Thus, Pauli was a behind the scenes participant in many discoveries in QM.

In August 1924, Pauli argued that angular momentum of the atomic nuclei is associated with a small magnetic moment that leads to hyperfine splitting of the atomic spectral lines in the presence of magnetic field. Then, to explain the anomalous Zeeman effect, in December 1924, he put forward the idea of a new quantum theoretic property of the electrons in an atom calling this 'two-valuedness not describable classically'. This unusual attribute of the electron not only increased the count of quantum numbers from three to four but also predicted the quantum nature of its magnetic moment and is now known as spin. Similarly, the nonzero nuclear magnetic moment has been found to be related to nonzero nuclear spin which may be an integer or a half integer. Furthermore, in January 1925, he proposed the stunning exclusion principle, which is named after him with abbreviation PEP and is subject matter of this article. This, in turn, explained the structure of atoms and their different properties in accord with their arrangement in the periodic table. Still, it was not accepted immediately and remained a topic of debate for quite some time.

It is pertinent to note that the three concepts mentioned in the preceding paragraph, particularly the last two with noteworthy consequences, emerged seemingly from nowhere based on his spectacular insight and were posited before the birth of QM. He did look for a deeper justification for PEP in later years. It may also be added that in the early months of second half of 1925, impressed by the idea of the fourth quantum number of the electron in PEP, Uhlenbeck and Goudsmit formally postulated spin as an intrinsic angular momentum of electron (assumed as a classical rotating charged sphere) spin having value $\hbar/2$ and this concept became finally acceptable only in 1928 when its correct interpretation was given by Dirac in the framework of relativistic quantum mechanics. In the meantime, in 1926, Pauli contributed an acclaimed review article on 'Quantum theory' in volume 23 of *Handbuch der Physik*. Soon after the discovery of matrix mechanics by Heisenberg in 1925, Pauli used it to explain the experimental data of the hydrogen spectrum, providing credibility to the new theory. Thus, this was his first formal contribution to the development of QM. In 1927, he considered the spin-half or two quantum degrees of freedom particles interacting with an external electromagnetic field in the framework of nonrelativistic QM by formulating the Schrödinger wave equation for these and introduced the $2 \times 2$ matrices (now named after him) as a representation of the three components of spin operator. The same year, he investigated the behaviour of the free conduction electrons (the spin-half particles) in alkali metals in the presence of an external magnetic field and explained the experimentally observed weak and temperature-independent paramagnetism of these metals. This phenomenon is now called Pauli paramagnetism. In fact, this work laid the foundation of modern theory of solids. He also presented the formulation of the grand canonical ensemble in quantum statistics in 1927.

In 1928, he together with Heisenberg and Jordan initiated the work on relativistic quantum field theory. In December 1930, he predicted the emission of a highly penetrating, electrically neutral and almost massless particle in the nuclear beta decay to account for their continuous energy spectrum. These hypothetical particles were later called neutrino by Fermi and were experimentally detected only in 1956. In 1933, he published a well-received review article entitled 'Principles of wave mechanics' in volume 24 of *Handbuch der Physik*. In 1934, he collaborated with Weisskopf to work on a problem on relativistic quantum field theory and showed that charged particles of spin zero have antiparticles of opposite charge – a finding that was applicable to the pions, discovered more than a decade later. Then, in 1940, while analyzing the symmetries in the quantum field theory, he derived the spin-statistics theorem establishing a relation between the spin of a particle and its statistical properties. Because of the importance of special relativity in proving this theorem, he considered this connection to be ‘one of the most important applications of the special relativity theory’. Also, in his Nobel Prize lecture, delivered on December 13, 1946, he called this ‘the law of nature’. It is worth adding that so far, no completely acceptable proof has been given for the spin-statistics theorem despite its being one of the most fundamental physical effects and the fact that many serious attempts based on a variety of assumptions have been made in this direction. In their book ‘Pauli and the Spin-Statistics Theorem’ published in 1998, Duck and Sudarshan wrote, “everyone knows the spin-statistics theorem, but no one understands it”.

During 1940-46, the focus of his research activity was on the meson theory. After his return to Zurich in 1946, he together with his students worked on different problems in quantum field theory and quantum electrodynamics. Some of his ideas were instrumental in the development of the standard model of particle physics in the second half of the 20th century. He spent most of his time after 1950 studying history and philosophy of science, looking for the relation between science and religion, and discussing these topics with others.

Everything that originated from his supremely great mind always bore a mark of his deep understanding and high quality. Based on his interactions with mystical psychologist Jung, he made significant contributions to psychiatry through his criticism of its epistemology, and zeal to understand physics and psychology as complementary aspects of the same reality. Interestingly, he also collaborated with well-known historian of art, Panofsky. In addition, in 1952, he published an exhaustive historical analysis of Kepler-Fludd debate on the scientific and hermetic approaches to understand nature of the Universe. In this essay, written in the language of Jung’s analytic psychology, Pauli appeared to indicate that studies in physics should be carried out with the attitude of ‘the alchemists of old’. These contributions together with those in physics bring out his multifaceted personality – in contrast with the usual hard rational traits of professional physicists.

We close this chronicle by mentioning the following.

i. The works listed here are not the complete story of research carried out by Pauli and there were many more contributions made by him to problems in theoretical physics.

ii. His general approach to doing physics was to develop experiment-inspired comprehensive intuition and construct a mathematically rigorous theory to prove his premise following the tenet 'mathematics describes reality more accurately than intuition'.

iii. His two hallmarks, ruthless rigour and perfectionist attitude in the harmonious description of the totality of a phenomenon, applied not only to his own work, but to the work of others as well. This made him to be referred to in the physics community as the 'conscience of theoretical physics'. He was also known for his acerbic remarks which spared none. Though his criticism was always sound, it was, sometimes, quite degrading and hurting. Despite all this, people remained his friends and took his biting sarcasms as inherent quality because they respected his unfettered brilliant creativity and highly valued his censorious opinion.

iv. Throughout his scientific life, Pauli was quite intrigued by the fact that the fine-structure constant, a dimensionless fundamental physical constant (introduced as an important parameter in the description of atomic structure by Sommerfeld in 1916 in the old quantum theory) that characterizes the strength of electromagnetic interactions between any two elementary charged particles such as electrons and protons, has a particular value nearly equal to 1/137. His obsession with this mysterious number, now considered as a coupling constant of nature, can be gauged by his statement "When I die my first question to the Devil will be: What is the meaning of the fine structure constant?"

## Appendix 3: Pauli – a Celebrated Author of Books

Pauli's article on special and general relativities in the *Encyclopedia of Mathematical Sciences* was later updated and published as a monograph. This book on 'Theory of Relativity' remains one of the masterpiece presentations of relativity theories. Also, both of his review articles in *Handbuch der Physik* (which contained thoughtful summarizing statements) too were brought out as books with titles 'Quantum Theory' and 'Principles of Wave Mechanics'. Both these books were classics on the subjects at that time. In addition to these, he published six volumes of collected lectures on physics (including 'Lectures on Continuous Groups and Reflections in Quantum Mechanics'), and two books entitled 'General Principles of Quantum Mechanics' and 'Meson Theory of Nuclear Forces'. His collaboration and correspondence with psychiatrist Jung resulted in two books 'The Interpretation of Nature and the Psyche' and 'Atom and Archetype - The Pauli/Jung Letters, 1932–1958'. Besides, his 'Writings on Physics and Philosophy' and selected 'Scientific Correspondence' also have been brought out in the form of books; surprisingly, the latter too has six volumes. The extent of all types of his printed work and bunches of still unpublished letters show that he was a prolific writer who could think only with a pen in his hand.

## Appendix 4: Views of Einstein, Born, and Gamow about Pauli [4,21]

i) Despite their severe disagreement on some fundamental issues in QM, Einstein had great respect for Pauli's ingenuity and called him his intellectual successor in his speech at the party held in Princeton to felicitate the latter for the award of Nobel Prize [21]. Also, he used to send his proposals on the unified field theories to Pauli seeking his discerning feedback.

ii) In an article published in 1969, Born wrote about Pauli: "Since the time when he was my assistant in Göttingen, I knew he was a genius, comparable only to Einstein himself. As a scientist he was, perhaps, even greater than Einstein. But he was a completely different type of man, who, in my eyes, did not attain Einstein's greatness" [21].

iii) In his book 'Thirty Years that Shook Physics', Gamow has written: "It is just as difficult to find the branch of modern physics in which the PEP is not used as to find a man as gifted, amiable, and amusing as Wolfgang Pauli was" [4].

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# Exploring the Anomalous Temperature Dependence of the Speed of Sound in water: An Undergraduate Ultrasonic Interferometry Experiment

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**Abstract**

A pedagogical approach through which students can investigate the anomalous behaviour of water through the temperature dependence of ultrasonic velocity using a simple ultrasonic interferometer experiment has been reported in the article. We examine the variation of the speed of sound in water and compare it with that in a commercially available groundnut oil. The measurements were performed using an ultrasonic interferometer operating at 1 MHz over a temperature range of 30–70 °C.

The speed of sound in groundnut oil exhibits linear decrease with increase in temperature, a trend commonly observed in liquids. In contrast, water exhibits a non-monotonic behaviour: the speed of sound initially increases with temperature, reaches a maximum, and subsequently decreases with further increase in temperature. This characteristic response reflects the competing effects of density and bulk modulus, governed by water's extensive hydrogen-bonding network.

The study not only highlights a fundamental acoustic property of liquids but also offers an engaging experiment for undergraduate students to explore water's anomalous behaviour and the molecular forces responsible for its unique characteristics.

## 1. Introduction

This study focuses on measurement of speed of sound, a property intrinsically linked to a liquid's density (ρ) and bulk modulus ($K$) through the fundamental relation $v=\sqrt{\frac{K}{\rho}}$. Both quantities $K$ and ρ are temperature-dependent, their independent variations may lead to linear or non-monotonic variation in the speed of sound as a function of temperature. The bulk modulus of liquids is governed by molecular structure and interactions.

We have studied speed of sound in water and a groundnut oil, as a function of temperature. We have established their different acoustic behaviours. It is a practical and easy way to understand and appreciate anomalous behaviour in water.

## 2. Experimental

The speed of sound in liquid samples is measured using an ultrasonic interferometer procured from Optiregion pvt ltd. The schematic diagram of experimental set up used for carrying out measurements is provided in Figure 1. In this set up, ultrasonic waves are generated using Quartz crystal at the bottom of a cylindrical cell of ultrasonic interferometer. The waves are reflected by a movable metallic reflector fitted in the cell, parallel to the crystal. The superposition of the incident waves of 1 MHz, gets reflected from the surface and results in standing wave. The movable reflector is attached with a screw gauge of 0.01 mm least count to facilitate the measurement of a position. The acoustic resonance is seen by electrical reaction on a generator driving the quartz crystal and results in increase in anode current of the generator. A position of ten to twelve successive antinodes is measured using screw gauge attached to the instrument. A difference between two alternate antinodes lead to wavelength. Thereafter, speed of sound is calculated using wavelength and frequency.

A high temperature water is circulating around the cell, for taking readings at higher temperature. A temperature was controlled with accuracy of ±1°C. After waiting for sufficient time to attain the temperature equilibrium higher temperature readings are recorded.

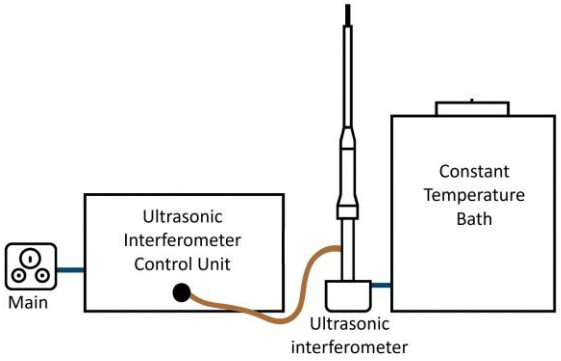

Figure 1: Schematic diagram of the experimental set up

## 3. Result and Discussion Conclusion

The speed of sound computed for the oil and water is exhibited in Figure 1 and 2 respectively. Figure 2 depicts that speed of sound in the oil decreases linearly with increase in temperature. Figure 3 exhibits that the speed of sound in water increases with initial increase in temperature, attends a maximum value and decreases with further increase in temperature.

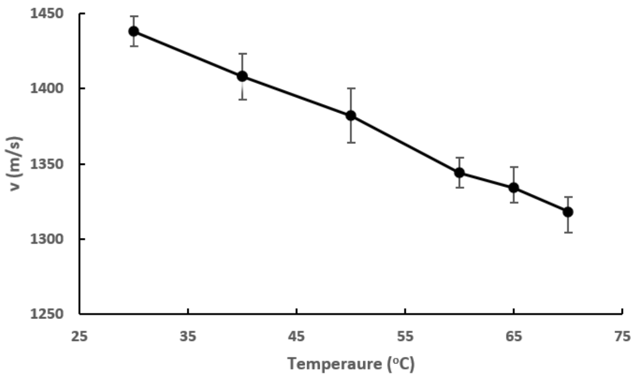

Figure 2: Speed of sound in the oil as a function of temperature

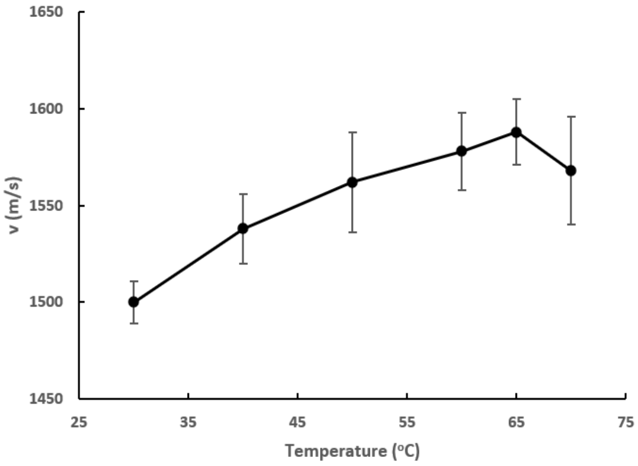

Figure 3: Speed of sound in water as a function of temperature

In general density of liquid decreases with increase in temperature [1]. Therefore, it is imperative that the difference in trend in speed of sound in water and oil is due to difference in variation in bulk modulus. In oil, compressibility increases with temperature because the thermal kinetic energy of the molecules rises, weakening the intermolecular forces. As a result, the liquid becomes easier to compress. Since the bulk modulus is the reciprocal of compressibility, an increase in compressibility implies that the bulk modulus decreases with increase in temperature. Because the decrease in bulk modulus with temperature is much larger in magnitude than the corresponding decrease in density, the speed of sound in the oil decreases as temperature increases. The trend observed in our measurements is consistent with results reported for other oils in the literature. [2] The anomalous behavior of speed of sound in water is probed since long time and is explained using two state theory. [3-5] The early seminal work has reported a trend in variation in compressibility as a function of temperature. [6-7] The anomalous change in bulk modulus has been of great interest since its discovery and addressed from inter molecular interactions perspective in the recent work. [8] It has been reported that the bulk modulus of water increases with initial increase in temperature, attains a maximum and decreases with further increase in temperature. This implies that with increase in temperature, speed of sound increases up to certain temperature and decreases with further increase in temperature.

An initial increase in the speed of sound with temperature, reaching a maximum value at a certain temperature, followed by a decrease with further temperature rise is in agreement with all reported literature.[3,5] The range of values of speed is in good agreement with the literature. However, a temperature at which the speed of sound is maximum at around 74–76 °C [3,5].

## 4. Conclusion

The present study demonstrates the anomalous temperature dependence of the speed of sound in water, in contrast to the behaviour observed in oil. In oil, the speed of sound decreases monotonically with an increase in temperature. However, in water, the speed of sound initially increases with temperature, attains a maximum, and subsequently decreases with further increase in temperature. Even without a detailed exploration of the temperature corresponding to the maximum sound speed and its subsequent decrease in water, the contrasting trends observed in water and oil are sufficient to establish the anomalous behaviour of water. These observations provide valuable insights into the variation of the bulk modulus with temperature and can be effectively incorporated as an undergraduate laboratory experiment. Further work is warranted to confirm the attainment of a maximum in sound speed at a specific temperature and its subsequent decrease at higher temperatures. Such confirmation would require experimental arrangements capable of operating at elevated temperatures with improved temperature control and measurement accuracy.

## Acknowlegements

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## Errata

There are two mistakes in the article 06 published in Volume 35, Issue 4.

1. Page 4, the caption for Figure 2. “$x_{\mathrm{L}} - x_{\mathrm{S}}$” should be “$x_{\mathrm{S}} - x_{\mathrm{L}}$”.
2. Page 5, the caption for Figure 4. “$x_{\mathrm{S}} - x_{\mathrm{L}}$” should be “$x_{\mathrm{L}} - x_{\mathrm{S}}$”.